REPUBLIC OF TURKEY
ERCIYES UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
DEPARTMENT OF MECHANICAL ENGINEERING

VALORIZATION OF SPENT COFFEE GROUNDS INTO BIODIESEL: BLENDING WITH ALCOHOLS, ENGINE PERFORMANCE AND FT-IR, TGA, DSC AND NMR CHARACTERIZATIONS

Prepared by
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M. Sc. Thesis

January 2020
KAYSERİ

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SCIENTIFIC ETHICS SUITABILITY

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ACCEPTANCE AND APPROVAL PAGE

This study entitled **"Valorization of Spent Coffee Grounds into Biodiesel: Blending with Alcohols, Engine Performance and FT-IR, TGA, DSC and NMR Characterizations"** prepared by Omar Khalid Mustafa AL-RUBAYE under the supervision of Asst. Prof. Dr. Abdulaziz Mohamed ATABANI was accepted by the jury as MSc. Thesis in Mechanical Engineering department.

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Omar Khalid Mustafa AL-RUBAYE

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ABSTRACT

Coffee is a global popular drink that is consumed in huge amount daily due to its refreshing properties. During the coffee making process, a dark brown waste known as spent coffee grounds (SCG) is generated. SCG is a valuable organic waste that is abundant worldwide. This waste has outstanding characteristics making it a promising resource to produce various types of biofuels and added-value products. This study aims to valorize this waste into biodiesel. Oil content of SCG has been found to be ~12% (by mass). The extracted oil (SCGO) has been found to have high acid value of ~24 mg KOH/g oil. Therefore, spent coffee grounds oil methyl ester (SCGOME) was synthesized through two steps of acid catalyzed process employing HCL followed by alkaline catalyzed transesterification processes employing KOH along with methanol and heating at 60 °C. It has been found that SCGOME satisfies the limit prescribed by ASTM D 6751 biodiesel standards with cetane number of 49.98, kinematic viscosity of 3.32 mm^2/s (at 40 °C), flash point of 137.5 °C, density of 891.9 kg/m^3 (at 15 °C), oxidation stability of 3.79 h and higher heating value of 39.11 MJ/kg. Physicochemical properties of SCGOME and its binary and ternary blends with Euro diesel and higher alcohols of butanol, pentanol and octanol were studied. Following this blending strategy, improvement in both density and cold flow properties where densities of the ternary blends were found very close to Euro diesel. Moreover, fast, cheap and reliable characteristics of DSC, FT-IR, UV-Vis, TGA and NMR were adopted in this work to evaluate the impact of butanol, pentanol and octanol addition into biodiesel-diesel blends. Such characteristics proved their quality and reliability. Finally, engine performance parameters of BP, BSFC and brake thermal efficiency and emissions characteristics of CO, CO_2, HC, NO_x and EGT were examined and proved the positive aspect of adding higher alcohols to biodiesel–diesel blends.

Keywords: Spent Coffee Grounds, Recycling of Waste, Biodiesel, Higher alcohols, FT-IR, UV-Vis, TGA, NMR, Engine and emissions test.

ALKOL, MOTOR PERFORMANSI VE FT-IR, TGA, DSC VE NMR KARAKTERİZASYONUYLA HARMANLAMA YÖNTEMİYLE ATIK KAHVETELVESİNİN BİYODİZEL'E DÖNÜŞTÜRÜLMESİ

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ÖZET

Kahve ferahlatıcı özelliklerinden dolayı günlük olarak büyük miktarlarda tüketilen dünya çapında popüler bir içecektir. Kahve yapım süreci esnasında, atık kahve telvesi (AKT) olarak bilinen koyu kahverengi renkte bir atık üretilir. AKT dünya çapında bol miktarda bulunan değerli bir organik atıktır. Bu atık çeşitli biyodizel türleri ve katma değerli ürünler üretme konusunda onu umut verici bir kaynak yapan göze çarpan özelliklere sahiptir. Bu tez çalışması bu atığı biyodizele dönüştürmeyi amaçlamaktadır. AKT'nin yağ içeriğinin ~12 mg KOH/g olarak bulunmuştur. Çıkarılan yağın (AKTY) ~24 mg KOH/g'lık (kütleye göre) yüksek asit değeri ihtiva ettiği tespit edilmiştir. Bu nedenle, atık kahve telvesi yağ metil esteri (AKTYME) metanol ile birlikte KOH kullanan alkalin katalize ester dönüştürme işlemlerinin takip ettiği HCL kullanan asit katalşze etme işlemi ve 60 ℃ derecede ısıtmadan oluşan iki aşama vasıtasıyla sentezlenmiştir. AKTYME 49.98'lik setan sayısı, 3.32 mm^2/s'lik kinematik viskozite (40 °C derecede), 137.5 °C derecelik parlama noktası, 891.9 kg/m^3'lük yoğunluk (15 °C derecede), 3.79 h'lik oksitlenme kararlılığı ve 39.11 MJ/kg'lık daha yüksek ısınma değerinden oluşan ASTM D 6751 biyodizel standartları tarafından belirlenen sınırı sağlamaktadır. AKTYME'nin fizyokimyasal özellikleri ve onun Euro dizel ve bütanol, pentanol ve oktanlı gibi yüksek alkollerle ikili ve üçlü karışımları incelenmiştir. Bu karıştırma stratejisini uygulayarak, üçlü karışımların yoğunluklarının Euro dizele çok yakın bulunduğu noktada hem yoğunluk hem de soğuk akış özelliklerinde ilerleme gözlemlenmiştir. Ayrıca, biyodizel-dizel karışımlarına bütanol, pentanol ve oktanol eklenmesinin etkisini incelemek için DAC,

FT-IR, UV-Vis, TGA ve NMR'nin hızlı, ucuz ve güvenilir özellikleri bu çalışmada kullanılmıştır. Son olarak, BP, BSFC'nin motor performans parametreleri ve CO, CO_2, HC, NO_x ve EGT'nin fren ısıl verimliliği ve emisyon özellikleri incelenmiş ve bu biyodizel-dizel karışımlarına yüksek alkolleri eklemenin olumlu yanlarını kanıtlamıştır.

Anahtar Kelimeler: Atık Kahve Telvesi, Atık Geri Dönüşümü, Biyodizel, Yüksek Alkoller, FT-IR, UV-Vis, TGA, NMR, Motor ve emisyon testi.

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NOMENCLATURE

A_i	: Percentage of fatty acid
ABE	: Acetone-butanol-ethanol
AV	: Acid value
AFC	: Average fuel consumption
AFRL	: Alternative Fuels Research Laboratory
AMME	: *Aleurites moluccanus* methyl ester
B	: Biodiesel
But	: Butanol
Bp	: Brake power
BSFC	: Brake specific fuel consumption
η_{th}	: Brake thermal efficiency
CI	: Compression ignition
CAMO	: Crude *Aleurites moluccanus* oil
CH	: Coffee husk
CHO	: Crude hemp oil
CN	: Cetane number
CO	: Carbon monoxide
CO_2	: Carbon dioxide
CP	: Cloud point
CFPP	: Cold filter plugging point
CS	: Coffee silverskin
CSO	: Crude safflower oil
D100	: Euro diesel
DSC	: Differential scanning calorimetry
DSCG	: Defatted spent coffee grounds
DU	: Degree of unsaturation
ρ	: Density

DI : Direct injection

EGT : Exhaust gas temperature

ERU : Erciyes University

FAC : Fatty acids composition

FAME : Fatty acids methyl ester

FFA : Free fatty acids

FP : Flash point

FT-IR : Fourier transform infrared spectroscopy

FW : Food waste

GC : Gas chromatography

HC : Hydrocarbons

HHV : Higher heating value

HME : Hemp methyl ester

ICE : Internal combustion engines

IV : Iodine value

KV : Kinematic viscosity

LCSF : Long chain saturated factor

LHV : Lower heating value

M_i : Molecular weight of each fatty acid

MB : Methylene blue

MG : Malachite green

MP_n : Melting point of each saturated fatty acid

N : Number of double bonds of fatty acid

NMR : Nuclear magnetic resonance

NO_x : Nitrogen oxides

Oct : Octanol

OS : Oxidation stability

Pen : Pentanol

PM	: Particulate matter
PP	: Pour point
SME	: Safflower methyl ester
SO_2	: Sulfur dioxide
SCG	: Spent coffee grounds
SCGO	: Spent coffee grounds oil
SCGOME	: Spent coffee grounds oil methyl ester
SCGOME/WCOME	: Spent coffee ground/waste cooking oil methyl ester
TG	: Thermogravimetry
TGA	: Thermogravimetric analyses
UV-Vis	: Ultraviolet–visible spectroscopy
WCO	: Waste cooking oil

INTRODUCTION

Recycling of waste whether organic or non-organic is a global issue that gets an increasing attention day by day. Recycling is considered as an act of responsible 'green' citizenship. Globally, coffee beverage is heavily consumed in a daily basis due to its refreshing properties making it a very popular product for consumers. Coffee is the second largest traded commodity after petroleum and the second most consumed beverage after water. Therefore, this industry is responsible for generating huge amount of organic waste annually. Coffee silverskin (CS), coffee husk (CH), peel, pulp and spent coffee grounds (SCG) are among the most popular waste generated from this industry. SCG is the solid residue (with fine particle size, high organic load and humidity) that is left over in the coffee making machine after the preparation of instant coffee beverage. It contains more than 100 useful organic compounds making it a promising waste for a multitude of sustainable products and services.

Production of biodiesel, as a renewable fuel, from waste has been under spot recently. This is due to the associated problems with edible oils (food versus energy conflict), non-edible oils (due to unavailability of enough lands and environmental sustainability concerns due to deforestation) and microalgae (still high production cost). It has been reported that 75% of biodiesel production comes from the price of feedstock alone. Therefore, synthesis of biodiesel from waste may cut down the cost remarkably. As SCG has an average oil content of ~12% (by mass), it can be valorized to produce biodiesel while the left over after oil extraction namely; defatted spent coffee grounds (DSCG) can be valorized in many other ways such as for biofuels production or value-added products. However, several characterizations have to be conducted to assess the quality of the extracted spent coffee grounds oil (SCGO) prior to converting it to fatty acids methyl ester (FAME) or spent coffee grounds oil methyl ester (SCGOME). These

include gas chromatography (GC), acid value (AV) or free fatty acids (FFA), kinematic viscosity at 40 °C (KV) and density (ρ) at 15 °C.

This research basically aims to valorize SCG into SCGOME. Firstly, fresh SCG were collected from coffee shops in Kayseri then dried followed by oil extraction and conversion to biodiesel. SCGOME was then blended with Euro diesel (D100) and some selected higher alcohols of butanol (But) ($C_4H_{10}O$), pentanol (Pen) ($C_5H_{12}O$), and octanol (Oct) ($C_8H_{18}O$) to form binary (SCGOME–D100) and ternary (SCGOME–D100–Pen/Oct/But) blends at different percentages. Afterwards, characterizations of SCGO, SCGOME and its blends with D100, But, Pen and Oct were conducted at our facility; **Alternative Fuels Research Laboratory (AFRL), Energy Division, Department of Mechanical Engineering, Erciyes University (ERU)**. Engine and exhaust emissions performance analyses were conducted in a single-cylinder, four stroke, naturally aspirated and compression ignition (CI) direct injection (DI) diesel engine. Additionally, differential scanning calorimetry (DSC), fourier transform infrared spectroscopy (FT-IR), ultraviolet–visible spectroscopy (UV-Vis), thermogravimetric (TGA) and nuclear magnetic resonance (NMR) analyses for all blends were also studied.

One of the main objectives of this research, besides recycling, was to shadow the light into equivalent tests such as DSC, FT-IR, UV-vis, TGA and NMR. These analyses are very promising, reliable, fast and above all cheap. The obtained results proved the reliability of these tests.

This research is part of the continuous activities of AFRL to promote waste recycling, save the environment, thinking green and raise the awareness in Turkey and ERU. The produced biodiesel has been tested and found to be in good quality with superior properties such as high oxidation stability (OS) and cetane number (CN) due to it low degree of unsaturation (DU). The formed binary (SCGOME–D100) and ternary (SCGOME–D100–Pen/Oct/But) were all found with comparable properties to fossil diesel which resulted in an acceptable and comparable engine and emissions performance.

CHAPTER 1

GENERAL INFORMATION

1.1 Overview

Discarding and reusing of goods and products are considered as integral parts of our lives. This is because the issues of bulk waste generation and dumping to landfills have become a real challenge to many countries. Waste recycling is considered globally as an act of responsible 'green' citizenship. The principle of returning waste to the production cycle, a process that came to be called recycling, has a much long history. However, recycling gained widespread public support from industry, politics and consumers few decades ago around 1970s [1].

Energy is vital for various economics across the globe aiming to achieve economic transformation and rapid development. Therefore, energy security has become an important parameter for many countries. Energy security includes various critical factors such as reliability, diversification and availability of energy supply sources besides the security of energy infrastructure. Many countries including Turkey are confronted with this challenge due to the fluctuating geopolitical environment our world faces today caused by military conflicts and terrorist attacks. It is also noteworthy to mention that half of the world's oil comes from six countries and half of the world's gas comes from three countries mostly located in certain parts of the world; the Middle East, North Africa, the Caucasus [2].

On the other hand, the harmful emissions emitted from internal combustion engines (ICE) such as soot, carbon monoxide (CO), nitrogen oxides (NO_x), hydrocarbons (HC), sulfur dioxide (SO_2) and carbon dioxide (CO_2) and particulate matter (PM) cause various environmental issues (such as global warming) and health concerns. All of which is due to the extreme burning of fossil fuel. It is still believed fossil

fuels continue to account for the majority of global energy consumption, constituting 86% of the total energy consumed in 2016 [3]. Therefore, production of alternatives fuels such as biofuels is currently being under the spotlight [4].

Biodiesel is one of the leading alternative fuels that is recognized globally as a clean source for energy. Biodiesel is defined as fatty acid methyl ester than can be derived from various resources such as vegetable oils, animal fats, microalgae and waste through transterification process. Biodiesel is a potential fuel to be used in CI diesel engine due to its similar properties to biodiesel. Biodiesel has relatively lower calorific value, higher CN, KV and ρ. Therefore, biodiesel has been reported to produce lower brake power (BP), higher brake specific fuel consumption (BSFC) and NO_x emissions. Since biodiesel has higher oxygen content (11% by weight) compared to diesel, burning of biodiesel reduced the emission of CO, SO_2, soot, HC and smoke. Some of the main features of biodiesel is that it is clean alternatives, scalable, renewable, ecological, biodegradable, non-explosive, non-flammable, non-toxic, lesser emissions, has lower sulfur and aromatic content, has higher lubricity and flash point (FP) and excellent combustion characteristics, does not contribute to global warming and can be produced through recycling of waste and thus save the environment [4-10]. The properties of biodiesel produced from various feedstocks such as edible and non-edible can be seen in [5, 6, 11-13]. While production of biodiesel from waste cooking oil (WCO) and food waste (FW) can be found in [14-19] and [20, 21].

Similar to biodiesel, alcohols such as methanol (CH_3OH), ethanol (C_2H_5OH), propanol (C_3H_7OH), butanol (C_4H_9OH) and pentanol ($C_5H_{11}OH$), hexanol ($C_6H_{13}OH$) and Octanol ($C_8H_{17}OH$) and etc. are getting attention recently in CI ICE. This is due to several factors such as alcohols lower the emissions of NO_x due to its high latent heat of vaporization that causes cooling effect in the combustion chamber. Besides, having a high oxygen content that ensure complete combustion and therefore, lower CO, HC and smoke emissions. However, alcohols further reduced the BP and increase the BSFC resulting in a relatively poorer engine performance [22-27]. Various fermentation pathways can be applied to produce alcohols from waste such as wood, forest residues, crops and lignocellulosic components of municipal waste [28]. The properties of various members of the alcohol family can be seen in [22]. Several publications reported the

properties of alcohols-diesel [28], alcohols-biodiesel [24], biodiesel-diesel [11, 12, 29], and alcohols-biodiesel-diesel blends [8, 23, 25, 29-32].

1.2 Research problem

As stated in previous sections, the issue of waste management has become a real concern for many countries. Waste such as SCG are generated in huge amount daily. Such types of organic waste causes real threat to the environment if not treated, recycled or disposed in an efficient manner. It is well known that direct disposal of organic waste causes the generation of methane. This is attributed to the inadequate amount of oxygen to be fully degraded. That is all added to the challenges that many governments are facing to find more landfills and the huge financial cost on taxpayers who run such landfills. SCG is considered as valuable waste due to its excellent characteristics and availability. One of the main potential recycling opportunities is to recycle SCG into biodiesel. Biodiesel has been accepted worldwide as renewable and clean fuel to be used in CI diesel engines. Given the fact that feedstocks represent 75% of biodiesel production cost, finding potential waste resource such as SCG for biodiesel production may protect the environment, save the economy of many countries depending on fossil fuel imports besides establishing some integrated biorefineries that are able to produce biofuels and products of added value in a sustainable manner. On the other hands, CI diesel engines are responsible for generating many harmful emissions to the atmosphere due to burning of fossil diesel. Therefore, applications of other oxygenated fuels such as alcohols have been under investigation recently as addition to alcohols to CI diesel engines may alleviate some harmful emissions such as CO, NO_X, HC and smoke. Therefore, treatment of waste and harmful emissions from ICE are some of the main challenges that our environment faces today. Therefore, these challenges have been considered in the research for both recycling SCG and application of higher alcohols.

1.3 Objectives

Given, the research background and recent problems associated waste generation and emissions from ICE, this research aim to achieve the following:

(1) Valorization of SCG through recycling it into biodiesel as useful and clean source of energy that may contribute to support the energy sector in Turkey

followed by assessing its quality against ASTM D6751 and EN 14214 biodiesel standards.

(2) Assessing the quality of the binary blend; B20D80 as a renewable fuel developed from blending SCGOME with fossil diesel.

(3) Application of higher alcohols of But, Oct and Pen along with biodiesel-diesel blends in some selected percentages to form ternary blends.

(4) Examining the physical and chemical properties of all blends such as ρ at (15-40 °C), cloud (CP), pour (PP)and cold filter plugging points (CFPP).

(5) Further assessment of the quality of all blends, fossil diesel, higher alcohols and SCGO by means of DSC, FT-IR, UV-Vis, TGA and NMR analyses as they are cheaper, faster and reliable methods. All of which also to establish solid background and comparative results with base fuel, fossil diesel

(6) Conduction of some important engine and emissions performance parameters of all blends.

1.4 Organization of thesis

This thesis has 4 chapters. Contents of each chapter is summarized as below:

Chapter 1 Offers general information about recycling of waste with emphasize on SCG as abundant waste for biodiesel production. This chapter also focuses on shadowing the light on energy and energy security, harmful emissions from ICE that causes climate change and global warming and application of biodiesel and higher alcohols in CI diesel engines. The study also reviewed some of the recent publications on recycling of SCG, properties of SCGO, quality of SCGOME besides the application of higher alcohols in CI diesel engines. Therefore, research overview, problem, objectives and the existing results in literature were all included in this chapter.

Chapter 2 Clarifies in detail the research methodology and design.

Chapter 3 Shows and presents all findings of the current study.

Chapter 4 Provides a discussion and analysis of these findings besides comparing the results with existing literature and giving a summary of the key findings to put forward some recommendations for the future work.

1.5 Literature survey

1.5.1 Overview of SCG recycling opportunities and potential of SCG for biodiesel production

The history of coffee dated back to 1000 years ago when it was first discovered in Ethiopia [33]. Coffee tree belongs to the family *Rubiaceae.* Brazil and Vietnam are the major coffee producers worldwide with around 40% of total coffee production [9]. Due to it is refreshing nature, coffee drink is a very popular product worldwide making it the second most popular product after petroleum and second consumed beverage after water. For instance, the UK drinks 95 million cups of coffee every day. Finland has the highest per capita coffee consumption (11.9 kg per capita). Therefore, this industry is responsible for generating huge amount of organic waste that causes threat to the environment if disposed directly without proper management. Among the waste generated from this industry, SCG stands among the most important waste from this industry. It is estimated half a million tons of SCG are discarded in the UK every year. SCG is the solid brownish residue left over following the preparation of instance coffee drink. This generated waste has high organic load with fine particle size and high humidity making it very susceptible to fast rotting if not treated in a good manner [9, 34, 35].

SCG is an oil-containing organic waste material that has a huge potential for biodiesel production [7-9, 12, 36-43]. Figure 1.1 and Figure 1.2 show some photos of SCG, DSCG, SCGO and SCGOME. The different in colors between SCG and DSCG is obvious due to lipid extraction (SCGO extraction). Depending on the geographical location, oil content of SCG has been reported to range between 7.5% (minimum reported) to 20.6% (maximum reported) with ~12% being considered as the average oil content of SCG. SCG contains more than 1000 individual compounds including proteins, carbohydrates, tannins, fibers, caffeine, cellulose, non-protein nitrogenous, fatty acids, amino acids, polyphenols, minerals lignin and polysaccharides [9]. Thus, apart from biodiesel, SCG can be valorized in various ways such as for biogas [44-49], fuel pellet [50], bioethanol [37, 51, 52], biohydrogen [36], and hydrocarbons [53, 54] production and added-value products. The opportunities of producing added-value

products from SCG are highlighted in Table 1.1 [9]. The full proposed bio-refinery of SCG industry can be seen in Figure 1.3 [9].

Biodiesel production from SCG involves collection and transportation of SCG, drying, oil extraction and characterization, and biodiesel production. One of the main advantages of SCGO is its high stability. This is due to the low DU of SCGOME. However, SCGO has been reported to have high AV [7, 52, 54-56]. Fatty acids composition (FAC) of SCGOME is mainly dominated by linoleic and palmitic acids followed by oleic, stearic and arachidic acids [36, 56-58].

SCGO (represented as triolein) ($C_{57}H_{104}O_6$) can be transesterified to methyl oleate ($C_{19}H_{36}O_2$) and glycerol ($C_3H_8O_3$) by the following reaction [59]:

$$C_{57}H_{104}O_6 + 3CH_3OH \rightarrow 3C_{19}H_{36}O_2 + C_3H_8O_3$$

Analyses of fuel properties of SCGOME indicated that KV ranges between 3.5-5.5 mm^2/s, ρ between 841-927 kg/m^3 and PP between -1 to 16 °C [9].

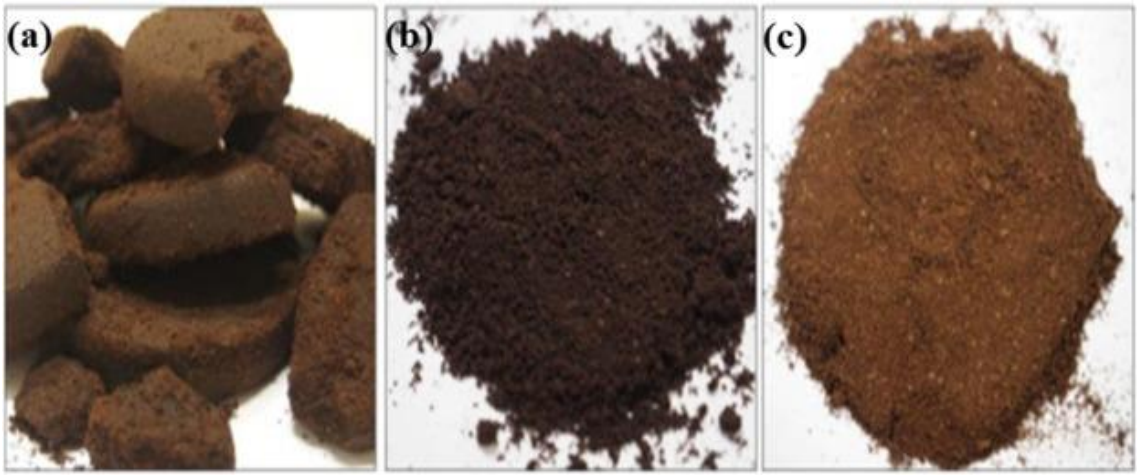


Figure 1.1. (a) SCG (b) Dried SCG (c) DSCG [9]

A summary of SCGO properties including its AV, FAC and properties of SCGOME and some other important aspects related to SCG such as elemental analyses, calorific value and chemical composition can be seen at [9].



Figure 1.2. SCGO (right) and SCGOME (left) [60]

Table 1.1. Opportunities of SCG recycling to added-value products [9]

Added-value product	**Source**		
Bioactive compounds & antioxidants	Bioactive compounds and antioxidants and anti-tumor activities		
Adsorbent	Water decontamination (removal of lead, methylene blue (MB), malachite green (MG), cationic and rhodamine dye and heavy metals, activated-carbon adsorbent, CO_2 adsorbent/capture (post-combustion), pesticide paraquat removal from aqueous solutions		
Textile	Wool fabrics dyed with spent coffee ground		
Sodium-ion battery	Facile preparation of pyrolytic carbon as anode		
Composting	Co-composting	Vermicomposting	Nanocomposites
Biopolymers	Odour control	Pulp and paper	Yarns
Creams-scrubs, soaps and detergents		Inks and screen painting	

Production of biodiesel (SCGOME) from SCG has been proposed in four main methods as [9]:

1- Direct transesterification with catalytic alkaline-based transesterification or acid-catalyzed esterification, methanol/CO_2 mixtures and enzymatic catalysis/biocatalyst such as *Candida rugose*, *Porcine pancreas*, *Pseudomonas fluorescens*, *Candida Antarctica* lipase-B *Mucor miehei*, *Pseudomonas cepacia*, *Rhizopus delemar*, *Thermomyces lanuginosus*, *Geotrichum candidum* and *Candida rugosa*.

2- Catalytic reaction of two steps of acid-catalyzed esterification followed by alkaline-based transesterification.

3- Non-catalytic transesterification.

4- *In-situ* transesterification.

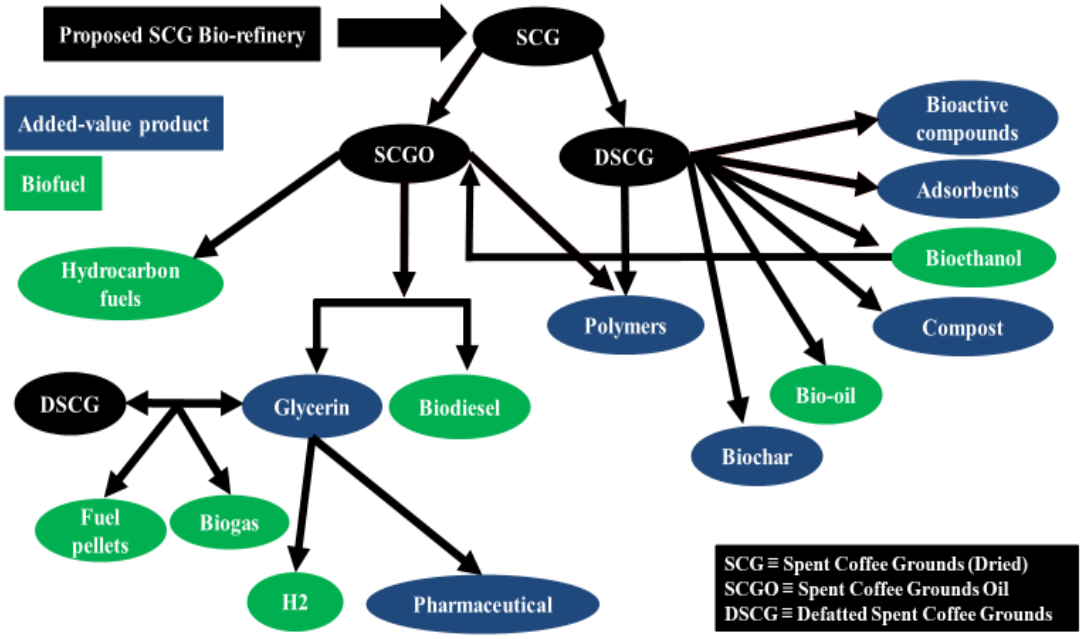


Figure 1.3. Proposed biorefinery of SCG [9]

1.5.2 Overview of alcohols application in CI engines

The properties of various members of the alcohol family can be seen in Table 1.2. The main characteristic of the alcohols, from the chemical point of view, is the presence of a hydroxyl group (–OH) attached to one of the carbons atoms of the molecule [61]. Several publications reported the properties of alcohols-diesel [28, 62-65], alcohols-biodiesel [24, 66, 67], and alcohols-biodiesel-diesel blends [8, 23, 25, 26, 29-32, 68-71] in CI diesel engines. It was proved that presence of alcohols in diesel engines improves combustion and reduces engine emissions as they have lower sulfur content and higher oxygen content than fossil diesel. However, this is accompanied with a penalty in BP and torque due to their lower energy content [28].

Butanol (C_4H_9OH) is an alcohol getting attention recently due to its renewable nature and more similar properties to diesel compared to ethanol and methanol for the application in ICE such as ρ, calorific value, CN and KV besides it is better miscibility with diesel. Moreover, it can be produced from biomass via ABE (acetone-butanol-ethanol) fermentation process. This process involves pretreatment of lignocellulosic biomass followed by detoxification and finally fermentation [61]. Application of But in CI diesel engines has been reported in many recent publications such as in [25, 30, 31, 61-65, 68, 70, 71].

Pentanol ($C_5H_{11}OH$) is a 5-carbon structure straight-chain alcohol. Compared to But, Pen has higher ρ, energy content, KV and FP relative to butanol. Thus, it is more suitable and attractive additive in diesel engines than butanol, ethanol and methanol respectively. The reported literature indicated that Pentanol be produced from glucose or glycerol by using the metabolic engineering of novel biocatalysts [27]. Application of Pen in CI diesel engines has been reported in many recent publications such as in [23, 27, 62, 72-74].

Octanol ($C_8H_{17}OH$), an 8-carbon straight-chain bio-alcohol grabbed the focus of researchers due to its properties closer to diesel and the possibility of its biosynthesis pathway from lignocellulosic biomass using engineered micro-organisms like Escherichia Coli and Clostridium species [75]. Application of Oct in CI diesel engines has been reported in [66].

Table 1.2. Comparison between alcohols, biodiesel and diesel properties [25, 27, 61, 66, 76, 77]

Properties	**Methanol**	**Ethanol**	**Propanol**	**Butanol**	**Pentanol**	**Hexanol**	**Octanol**	**Biodiesel**	**Diesel**
Molecular weight	32.04	46.06	60.1	74.12	88.15	102.18	130.23	a	198.4
CN	3	8	12	25	18.2-20	23	39	56	52
Lower heating value (LHV) (MJ/kg)	20	26.83	30.6	33.09	34.65	39.10	37.512	37	42.5
Latent heat of vaporization (kJ/kg)	1162	918	727.9	626	308.05	486	298	300	260
Carbon (by wt. %)	37.5	52.2	60	64.82	68.13	70.52	73.72	77.1	84-87
Hydrogen (by wt. %)	12.6	13.1	13.4	13.49	13.61	13.70	13.82	12.1	13-16
Oxygen (by wt. %)	50	34.8	26.6	21.6	18.15	15.70	12.29	10.8	0
ρ at 15 °C (kg/m^3)	791.3	789.4	803.7	809.7	814.8	821.8	827	880-900	835
KV at 40 °C (mm^2/s)	0.59	1.08		2.63	2.88	4.5	7.3	3-6	1.9-4.1
Self–ignition temperature (°C)	463	420	350	345	300	285	270	271	254-300
FP (°C)	11	14	22	35	49	59	81	a	74
C/H mass ratio	–	3.97	–	4.77	4.96	–	–	–	6.46

[a] molecular weight and flash point of biodiesel varies depending on type of feedstock and fatty acids compositions

CHAPTER 2

MATERIALS AND METHODS

Research methodology is a vital research element in which it comprises the specific materials, theory, procedures or techniques used to identify, select, process, analyze and carry out the specific research. This chapters describes, in details, the conditions by which fresh SCG were collected, dried and stored prior to oil extraction at AFRL, ERU. This was followed by characterizing the extracted oil (SCGO) and synthesis of biodiesel (SCGOME). All materials and chemicals needed to produce biodiesel besides alcohols and Euro diesel were also highlighted. Furthermore, quality, reliable, fast and cheap methods such as FT-IR, UV-vis, TGA, DSC and NMR analyses were also adopted in this work. This is to assess the quality of the developed binary blends (biodiesel–diesel) and ternary blends (biodiesel–diesel–alcohols). At the end, some selected engine and emissions performance parameters were also concluded in this research.

2.1 Structure of research methodology

As mentioned earlier, this research aims to valorize organic waste through recycling of SCG followed by oil extraction (SCGO) and converting it to biodiesel (SCGOME). An additional aim of this research is to study the application of higher alcohols of But, Pen and Oct along with SCGOME and D100 in binary and ternary blends CI diesel engines. Figure 2.1 summarizes the flow and adapted research methodology.

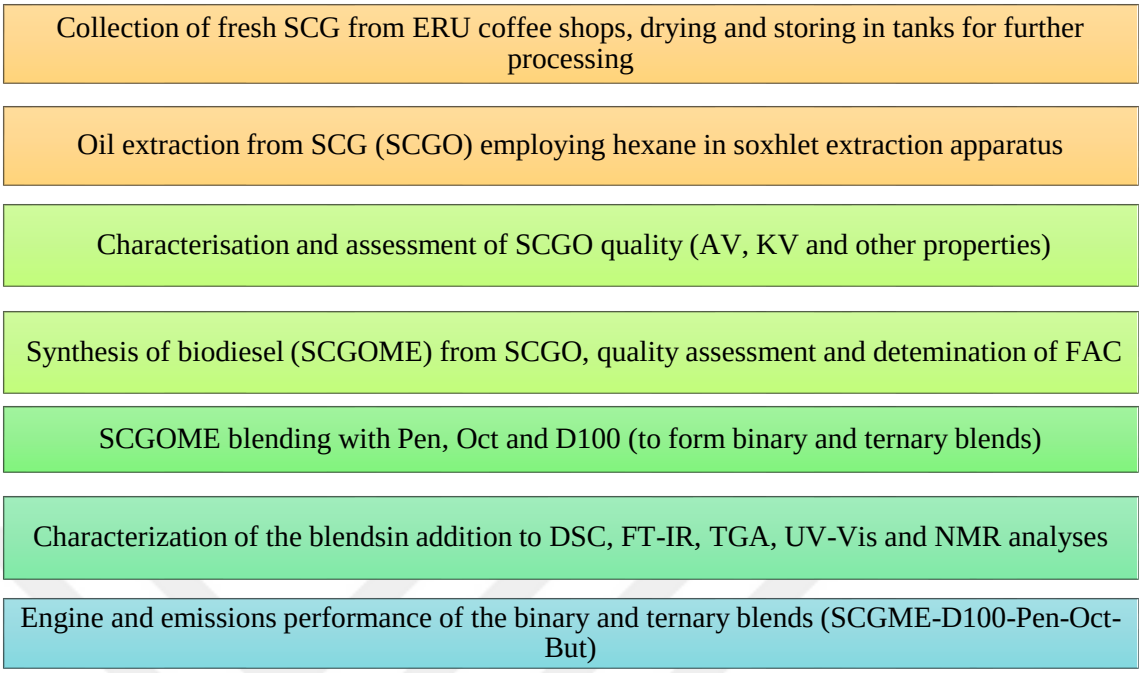


Figure 2.1: Summary of current research methodology

2.2 Collection of SCG

As has been stated in the previous section and Chapter (1), recycling of organic waste and proving the unlimited benefits of valorizing them into biofuels and value-added products was one of the main aims of this research. In this study, fresh SCG samples were collected from some coffee shops inside ERU campus. Emphasize was made on collecting only fresh SCG in good conditions to avoid rotten samples that have a deteriorated quality and thus negatively affect the output of this study. Upon collection, wet SCG were immediately placed in an oven (Model: Mikrotest, MKD serisi, Turkey) and dried at 105 °C to remove moisture. The dried SCG were then removed and stored in tanks and closed well to avoid contact with air.

2.3 Extraction of SCGO from SCG

Weighed fresh and dried SCG samples were placed in a soxhlet extractor unit comprised of heater with ceramic magnetic stirrer (ISOTEX, SH4, Analog, maximum speed 2000 rpm, maximum temperature 380 °C, Turkey), flask (1000 ml, S & H labware, USA), extractor (500 ml, S & H labware, USA), condenser (S & H labware, USA) and refrigerated bath circulator (JS Research Inc, JSRC-13C, South Korea). Hexane (C_6H_{14}) was used as a solvent with heating at 70 °C. Upon completion of the

extraction process, the extracted amount of SCGO along with the hexane were transferred to a rotary evaporator unit (Hahnshin Scientific Co, Hahnvapor, HS-2005V-N, South Korea) attached with water bath (Hahnshin Scientific Co, Hahnvapor, HS-3001 (PTFE coating)), vacuum pump (Rocker Scientific Co., Ltd, Chemker410, Taiwan) with vacuum pressure of 760 mmHg and refrigerated bath circulator (JS Research Inc, JSRC-13C, South Korea) to separate hexane from SCGO so the hexane can be used back again in the next extraction cycle. The amount of extracted SCGO was then weighed to calculate the oil content of SCG (Equation 1) and then stored in bottles and kept in shelves to avoid contact with both air and sunlight. It has been found that the oil content of SCG is ~12% (by mass). This finding is in agreement with [7, 41, 50, 54, 58, 78-84] respectively.

$$Oil\ content\ of\ SCG\ \left(\%\frac{m}{m}\right) = \frac{mass\ of\ SCGO\ (g)}{mass\ of\ SCG\ (g)\ (dry\ basis)} \times 100 \quad (\mathbf{1})$$

2.4 Chemicals

All chemicals used in this research such as n-butanol (C_4H_9OH) (CAS-No: 71-36-3) (MW: 74.12 g/mol), n-pentanol ($C_5H_{11}OH$) (CAS-No: 71-41-0) (MW: 88.15 g/mol), n-octanol ($C_8H_{17}OH$) (CAS-No: 111-87-5) (MW: 130.23 g/mol), methanol (CH_3OH) (CAS-No: 67-56-1) (MW: 32.04 g/mol), n-hexane (C_6H_{14}) (CAS-No: 110-45-3) (MW: 86.18 g/mol), sodium sulfate (Na_2SO_4) (CAS-No: 7757-82-6) (MW: 142.04 g/mol), hydrochloric acid (HCL) (CAS-No: 7647-01-0), potassium hydroxide (KOH) (CAS-No: 1310-58-3) (MW: 56.01 g/mol) were of analytical grades and used as received from the suppliers. Qualitative filter papers (ADVNTEC, Toyo Roshi Kaisha, Ltd, Japan) were purchased from a local supplier in Kayseri, Turkey. Euro diesel was purchased from a local fuel station (OPET, Kayseri, Turkey).

2.5 Production of SCGOME from SCGO

AV of SCGO was determined and found to be ~24 mg KOH/g oil. This result indicates the extremely high AV of SCGO. However, this is similar to [7]. Moreover, most of the published work on SCG indicates its high acidity. Therefore, two steps of acidic esterification (using acid catalyst) to reduce the acidity of SCGO and convert the FFA into FAME followed by alkaline transesterification (using alkali catalyst) to convert the

triglyceride into FAME were adopted to produce SCGOME as single alkaline transesterification is impossible to process SCGO (having AV higher than 4 mg KOH/g oil). Table 2.1 shows the summary of biodiesel production process. This process resulted in a high quality final product with a biodiesel yield of more than 95%. The final product was reported to be in brownish colour.

Table 2.1. Summary of SGOME production process

Esterification	**Parameter**
HCL	1% (v/v oil)
CH_3OH	100% (v/v oil)
Reaction time	3h
Reaction temperature	60 °C

Transesterification	**Parameter**
KOH	1% (m/m oil)
CH_3OH	25% (v/v oil)
Reaction time	1.5h
Reaction temperature	60 °C

2.6 Equipment list

Table 2.2 summarizes the equipment used in this study including their manufacturers, origin, ASTM standard method and accuracy. All these units are available in AFRL, ERU.

Prediction of saponification number (SN) of SCGOME was made from the following empirical formula [8, 11, 25]:

$$SN = SUM\left(\frac{560*A_i}{MW_i}\right) \quad (2)$$

Where, A_i is the percentage and MW_i is the molecular mass of each fatty acid.

Other properties such as kinematic viscosity at 40 °C (KV), iodine value (IV), CN and OS of SCGOME were predicted by the following empirical formulas [8, 25, 31, 85]:

$$\ln(\eta_i) = -12.503 + [2.496 \times \ln(MW_i] - (0.178 \times N) \quad (3)$$

$$IV = 1.0617(DU) - 10.805 \quad (4)$$

$$CN = -0.1268(DU) + 67.926 \quad (5)$$

$$OS = -0.0518\,(DU) + 11.121 \quad (6)$$

Where η_i represents the KV of each fatty acid at 40 °C and DU is the degree of unsaturation which is calculated from the following formula [25, 30, 31, 85]:

$$DU = (monosaturated\ C_n{:}\ 1, wt\%) + 2(polunsaturatedC_n{:}\ 2, wt\%) + 3(polyunsaturated\ C_n{:}\ 3, wt\%) \quad (7)$$

Long chain saturated factor (LCSF) was calculated from the following formula [8, 26, 28, 71]:

$$LCSF = \sum \frac{(MPn * A_i)}{100} \quad (8)$$

Where, MP_n is the melting point and A_i is the percentage of each saturated fatty acid.

Higher heating value (HHV) of SCGOME was predicted by the following empirical formula **[30, 85]**:

$$HHV = 46.19 - \left(\frac{1794}{MW_i}\right) - (0.21 \times N) \quad (9)$$

Where N represents the number of double bonds of fatty acid.

Table 2.2. Equipment list

Property	**Model**	**Manufacturer**	**Origin**	**ASTM standard**	**Accuracy**
Kinematic viscosity (KV)	TV2000-AKV	PM Tamson Instrument	Bleiswijk, Netherlands	D445	±0.1 K
Cloud point (CP)	NTE 450	Normalab	Valliquerville, France	D2500	± 0.1 °C
Pour point (PP)	NTE 450			D97	± 0.1 °C
Cold filter plugging point (CFPP)	NTL 450			D6371	
Density (ρ)	DS7800	A.Krüss Optronic GmbH	Hamburg, Germany	D1298	±0.0001 g/cm^3

2.7 Gas chromatography (GC) method of SCGOME

GC is a technique for the analyses of FAME of lipids. The FAC profile of SGCOME was determined using gas chromatography (GC) (Agilent Technologies 7890 A GC System) equipped with a flame ionization detector (FID). The test was conducted using

an optimized in-house GC method [86]. Analysis were made as for standard of Fat and oil derivatives (FAME) Determination of ester and linolenic acid methyl ester contents. It is called as TS EN 14103. The carrier gas was hydrogen with column flow rate of 1.00 mL per minute. The detector temperature was 250 °C.

2.8 NMR analysis

NMR spectroscopy was first introduced by Isidor Rabi in 1938 [87]. This technique is widely used in many areas of science [88]. NMR spectroscopy is a well-established technique used for the identification and structure interpretation of chemical compounds. It has become a universal method in lipid analysis. NMR spectroscopy is rapid (can be done in less than 5 minutes for one sample), reliable and non-destructive technique for the analysis of oils and fats [89, 90]. This is attributed to its versatility and ability to provide unique information. The main advantage of this method is that it is capable of studying structural features (no any other technique can compete in this area). Some of the other main features of NMR spectroscopy are as follow [89]:

1. No calibration is required with internal standards.
2. Separation of various components prior to the analysis is not required.
3. It is qualitative as well as quantitative analysis that could be carried out with excellent repeatability and reproducibility.
4. It has ability to perform diverse studies on a single spectrum.
5. It is an efficient technique to identify different nuclei (multinuclear NMR).
6. It can easily distinguish geometrical isomers. ^{1}H and ^{13}C are widely studied in the field of lipid analysis.

NMR analyses of SCGO and its methyl ester (SCGOME), But100, Oct100, Pen100, D100, binary blend (B20D80) and ternary blends (D80But10B10, D80Oct10B10, D80Pen10B10) were performed using Bruker 400 NMR at 400 MHz (^{1}H) and 100 MHz (^{13}C) with the residual solvent peaks as internal references. A spectrometer equipped with suitable probes for cores of ^{1}H, ^{13}C, ^{19}F, ^{31}P. $CdCl_3$ was used as both the solvent as well as internal standard respectively. ^{1}H and ^{13}C spectra were recorded.

2.9 FT-IR analysis

FT-IR is a powerful technique for recognizing different types of chemical bonds, make-up or functional groups present in a molecules or samples (whether organic or inorganic). This is achieved by producing an infrared absorption spectrum as a molecular "fingerprint" [91-93].

The FT-IR spectra of SCGO and its methyl ester (SCGOME), But100, Oct100, Pen100, D100, binary blend (B20D80) and ternary blends (D80But10B10, D80Oct10B10, D80Pen10B10) were recorded using a Perkin Elmer in the range 4000-650 cm^{-1} and processed with a computer software program spectrum. The resolution was 4 cm^{-1} and 4 scans.

2.10 UV-Vis analysis

UV-Vis spectroscopy is another technique that has been used extensively in analytical chemistry for characterization, identification and quantitative analysis. It is a fast, simple and inexpensive method to determine the concentration of an analyte (compound to be analyzed) in solution. Therefore, it can be used for relatively simple analysis, where the type of analyte is known, to do a quantitative analysis to determine the concentration of the analytes. UV-Vis spectra provide information about the electronic properties of molecules [94]. All organic compounds absorb light in the visible and ultraviolet region [95, 96]. UV-Vis characterization to obtain UV absorption spectra for SCGOME, D80But10B10, D80Oct10B10, D80Pen10B10 and D80B20 was conducted using Agilent Technologies Cary 60 UV-vis Spectrophotometer, USA in the wavelength range of 800–300 nm at 1 nm intervals and scanned using standard 1 cm quartz cuvettes filled with the tested fuel at room temperature.

2.11 TGA analysis

Thermogravimetry (TG) is a technique developed nearly at 1900 in which the mass of a sample is monitored against time and linearly varying temperature in a given atmosphere. TG is performed with a TGA or thermobalance. TGA is an analytical technique used to determine a material's thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a sample is heated at a constant rate. A plot of mass as a function of time or temperature is the result of a

thermogravimetric experiment. TGA has emerged as an alternative, less expensive, fast and easier technique recently in biofuels industry [97, 98].

TGA analyses of SCGOME, But100, Oct100, Pen100, D100, binary blend (D80B20) and ternary blends (D80But10B10, D80Oct10B10, D80Pen10B10) were obtained using an Exstar 6000/6300 thermal analyzer (temperature range: room temperature to 1500 °C) using platinum (Pt) pans in which nearly 20 mg of each sample was placed in the pan. After each analysis, the Pt pans were cleaned well in order to make the pans ready for the next run. Each sample was heated over the temperature range of 25–700 °C at a heating rate of 10 °C/min under dry air (100 ml/min). Each test takes almost an hour. A maximum temperature of 700 °C was used as the mass remains constant until the end of analysis and all the chemical reactions have been completed at this temperature [99]. TGA curves were used to analyze the onset temperature of all samples.

2.12 DSC analysis

DSC is a thermal analysis technique in which the heat flow into or out of a sample is measured as a function of temperature or time, while the sample is exposed to a controlled temperature program. It is a very powerful technique to evaluate material properties such as glass transition temperature, melting, crystallization, specific heat capacity, cure process, purity, oxidation behavior, and thermal stability. DSC is characterized by its usefulness for analyzing phase changes. It is a well-established measuring method that is utilized on a large scale in different areas of research, development, and quality inspection and testing [100].

DSC analyses were performed to investigate the crystallization onset temperature of SCGO, SCGOME, But100, Oct100, Pen100, D100, binary blends B20D80 and ternary blends (D80But10B10, D80Oct10B10, D80Pen10B10). The DSC curves were obtained in Perkin Elmer model DSC 8500 equipped with a cooling system (temperature range -180–750 °C). Cooling rate was 10 °C/min under inert nitrogen atmosphere (N_2) with a flow rate of 20 mL/min. Each sample was 3±0.5 mg. Each DSC test takes about 16 mins to complete a single sample.

2.13 Engine specifications and emission device

Ricardo E6 (Figure 2.2) engine instrumentation were used to test SCGOME and its binary and ternary blends with D100, But, Pen and Oct. The set-up contained single cylinder CI diesel engine with water-cooling system, vertical type DI and coupled with an electric brake dynamometer. An electronic control and measurement device was used to display performance data. The schematic diagram of the set-up is shown in Figure 2.3. Table 2.3 lists the specifications of the engine and exhaust gas analyzer. All experiments were conducted at a fixed engine speed of 1800 rpm at different three loads of 0, 7.5, 11.5, 16, 19 and 21.5 N.m respectively.



Figure 2.2. Tecquipment photo

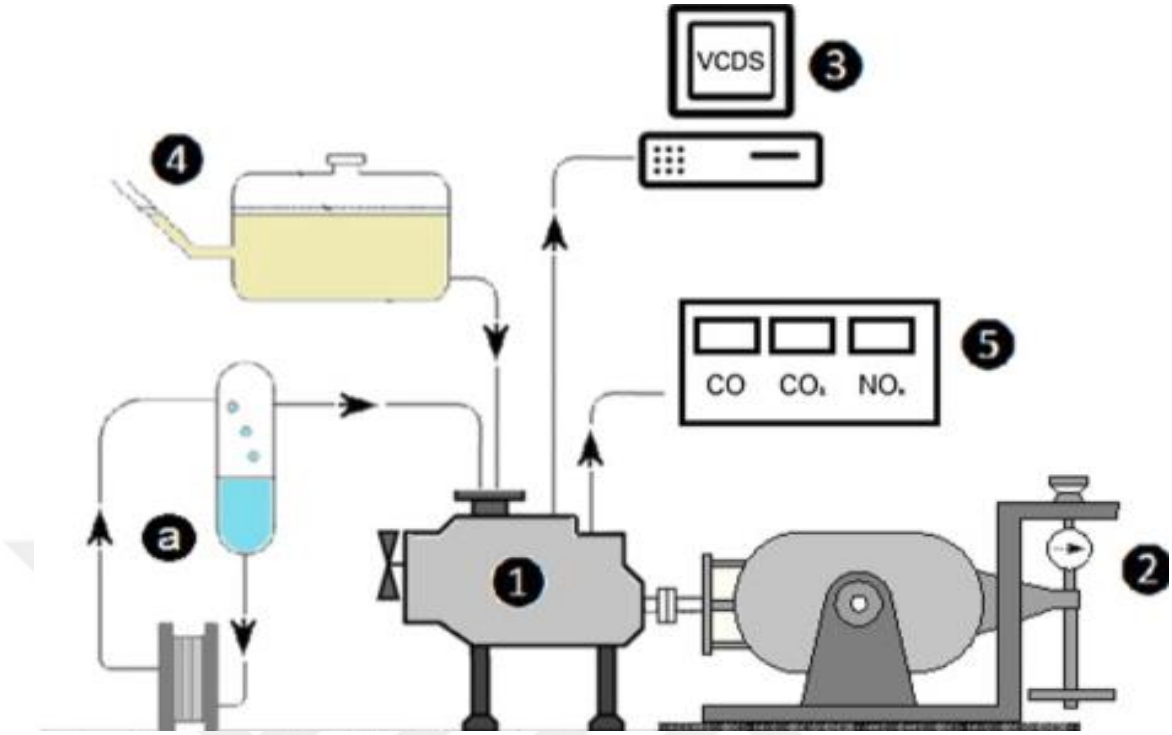


Figure 2.3. Schematic Diagram of the Test Engine

1- Engine; 2- Dynamometer; 3- Control unit; 4-fuel tank; 5 -Exhaust gas analyzer

Table 2.3. Engine and exhaust gas analyzer specifications

Item	**Technical specification**
Model	Ricardo E6
Type	Single-cylinder, vertical, 4-stroke water-cooled, DI CI diesel engine
Bore x stroke (mm)	76×111
Displaced volume (cc)	507
Rotary direction of Crankshaft	Clockwise from flywheel end
Cooling type	water-cooled system
Compression ratio	17/1

AIRREX GAS ANALYZER

Measurement: HC, CO, CO_2, O_2, NO_x, Lamda, AFR Measuring Method: HC, CO, CO_2: NDIR (Non-dispersive Infrared) O_2, NO_x: Electro Chemical Sensor
Gas Flow: 2~4 liter/min
Power Supply: AC 110/220V, 50/60Hz
Measure Range (Resolution) and accuracy CO: 0~9.999% (0.001%) : CO_2: 0~20.00% (0.015) HC: 1~15,000 ppm (1ppm) O_2: 0~25.00% (0.01%) NO_x: 0~5,000ppm (1ppm) Lamda:0.50~3.00 (0.01) Exhaust gas temperature (EGT): 200+1300 (±1)

CHAPTER 3

TESTS AND RESULTS

3.1. Introduction

In this chapter, FAC of SCGOME, physico-chemical properties of SCGO, SCGOME, D100 and binary and ternary fuel blends with D100, But, Pen and Oct are presented and compared with some existing results in the body of literature. This is followed by presenting the results of FT-IR, TGA, UV-Vis, NMR and DSC characteristics. Finally, some important engine and emissions performance parameters at different loads and fixed speed (1800 rpm) are presented and analysed.

3.2. Properties of SCGO, SCGOME, D100 and binary and ternary fuel blends

The difference in the chemical structures of biodiesel, diesel and alcohols results in differences in their basic properties such as KV, CN, IV, OS, HHV, FP, CP, PP and ρ and etc. Therefore, it is vital to measure these properties before burning them in CI diesel engines [101].

Tables 3.1-3.3 shows some of the basic physico-chemical properties of SCGO, SCGOME, D100 and SCGOME binary and ternary blends with D100, But, Pen and Oct respectively.

The results of AV, CP, PP and ρ (15-40 °C) of SCGO were compared with the results presented in [7, 102] for SCGO and [25, 30, 31, 86, 103] for some edible and non-edible biodiesel feedstocks such as safflower, hemp, *Aleurites moluccanus, Croton megalocarpus* and *Pangium edule , Ceipa pentandra* and *Nigella sativa* oils. The results of AV of SCGO were found similar to [7] (22.3 mg KOH/g oil) and higher than [102] (14.65 mg KOH/g oil). It shall be noted that the AV obtained in this results is quite

acceptable as it has been reported that the AV values of SCGO range between ~6 mg KOH/g oil and ~40 mg KOH/g oil [3]. AV was also found higher compared to most of feedstocks covered in this study [25, 30, 31, 86, 101, 103] except for *Calophyllum inophyllum* oil (41.74 mg KOH/g oil) [103] and *Nigella sativa* oil (30.35.74 mg KOH/g oil). These results also reveal that SCGO is less dense and has higher CP and PP than all other feedstocks presented in this work.

The obtained properties of SCGOME are in good agreement with ASTM D6751 standards regarding KV, CN, ρ, FP and OS. These properties were further justified following the FAC, DU and LCSF of SCGOME (Section 3.4). Therefore, biodiesel from SCG can be considered as a promising renewable fuel that can be exploited as a fuel in CI diesel engines. For better insight, these properties were also compared with those available in literature for some previous SCGOME studies [7, 102] and other feedstocks [7, 11, 25, 30, 31, 86, 101, 102]. The HHV of SCGOME obtained from this study is similar to [3] (39.72±0.428 MJ/kg), [7] (40.32 MJ/kg) and [102] (38.4 MJ/kg). The result is also comparable to other feedstocks mentioned in Table 3.2 [7, 11, 25, 30, 31, 86, 101, 102].

Density is the mass per unit volume [4]. This is one of the most important fuel properties as it affects the performance of CI diesel engine. This is because CI diesel engine injection systems operate on a volume metering system [3]. It is normally tested between 15 and 20 °C. Through Tables (3.1- 3.3), it can be seen that ρ of SCGO has been much improved through biodiesel production process to SCGOME in which ρ reduced from 920.6 to 891.90 kg/m^3 at 15 °C. The results of ρ obtained in this work is comparable to that of [102] (891.5 kg/m^3), [56] (892 kg/m^3) and [50] (894.3 kg/m^3). ρ of SCGOME has been further reduced when it was blended with D100 (binary blends) and D100, Pen and Oct (ternary blends) where ρ ranges between 842.4-850.2 kg/m^3 for all blends compared to 840.5 kg/m^3 (D100), 815.5 kg/m^3 (But), 819.8 kg/m^3 (Pen) and 830.8 kg/m^3 (Oct). It has been found that D80But10B10 has the closest ρ to D100 (842.4 kg/m^3). These results indicated the positive effect in reducing the ρ when blending higher alcohols (But, Pen and Oct) with diesel-biodiesel blends and, therefore, may contribute to boost engine and emissions performance. Moreover, the next section discusses the effect of temperature variations on ρ of all fuel samples.

CP, PP and CFPP are important properties that determine the flow of any fuels at low temperature. This is more importantly at cold regions where full or partial solidification of the fuel may cause blockages of fuel lines, filters and pumps. All of which leads finally to engine damage [4]. The cold flow properties of SCGOME including CP, PP and CFPP were 11, 12 and 5 °C respectively indicating that the use of 100% SCGOME as a fuel is not suitable in cold flow regions. Even SCGO has better cold flow properties than SCGOME (6 and 4 °C respectively). Therefore, blending SCGOME with D100, But, Pen and Oct remarkably improve these properties (CP: -3−-4 °C for blends compared to 11 °C of SCGOME), (PP: -8−-16 °C for blends compared to 12 °C of SCGOME) and (CFPP: -16−-24 °C for blends compared to 5 °C of SCGOME) indicating the positive strategy of blending with higher alcohols.

3.3. Effect of temperature variations on density (ρ) of fuel samples

In this work, an attempt to investigate the effect of temperature variation (15-40 °C) on the ρ of SCGO, SGOME, D100, But100, Pen100, Oct100, binary blends of D80B20 and ternary blends of D80B20, D80But10B10, D80Pen10B10, D80Oct10B10 was made. Table 3.4 shows the detailed results obtained in this study. Such approach helps predict the ρ of each fuel blends. As can be seen in Figure 3.1 (a-c), all developed correlation were leaner between the ρ and the temperature of the sample. All equations show high accuracy. Therefore, these equations can be used to predict the ρ at any temperature.

Table 3.1. Physico-chemical properties of SCGO

Property	**SCGO**	**SCGO [7]**	**SCGO [102]**	**CSO [25]**	**CAMO [30]**	**CHO [31]**	**CPEO [86]**	**CCMO [103]**	**CCPO [101]**	**CNSO [101]**
AV (mg KOH/g oil)	24	22.3	14. 65	0.505	10.68	3.857	19.62	12.07	20.23	30.35
CP (°C)	6	26	10	-14	-13	-11	-6		-7	7
PP (°C)	4	21		-22	-17	-22	-10		-3	-7
ρ at 15 °C (kg/m^3)	920.6	930.9	933.8	925.0	924.90	927.90			921.6	924.7
ρ at 20 °C (kg/m^3)	916.9	924.5		921.0	923.0	923.10				
ρ at 25 °C (kg/m^3)	913.3									
ρ at 30 °C (kg/m^3)	909.7									
ρ at 40 °C (kg/m^3)	902.7	917.6					897. 6	910	904.4	907.9

CSO ≡ Crude safflower oil, CAMO ≡ Crude *Aleurites moluccanus* oil, CHO ≡ Crude hemp oil, CPEO ≡ Crude *Pangium edule* oil, CCMO ≡ Crude *Croton megalocarpus* oil, CCPO ≡ Crude *Ceipa pentandra* oil, CNSO ≡ Crude *Nigella sativa* oil.

Table 3.2. Physico-chemical properties of SCGOME

Property	**SCGOME**	**SCGOME [7]**	**SCGOME [102]**	**SME [25]**	**AMME [30]**	**HME [31]**	**PEME [86]**	**CMME [11]**	**CPME [101]**	**NSME [101]**	**ASTM D6751**
CP (°C)	11	26	14	-2	-6	3	-6	-3	3	-1	-
PP (°C)	12	13		-7	-5	-4	-4	-2	5	-1	-
CFPP (°C)	5			-12	-8	-10	-8	-4	4	-4	-
FP (°C)	137.5	169.0	222	176	>224	180		164	202.5	172.5	Min 120
KV at 40 °C (mm²/s)	3.32	5.789	5.26	4.017	3.85	3.87	5.23	4.07	4.418	4.5026	1.9-6.0
HHV (MJ/kg)	39.11	40.32	38.4	40.60	39.38	40.413	39.625	39.786	40.064	39.967	-
CN	49.98	71.2		47.21	45.05	51. 63	47				47 min
IV (g iodine/100g)	139.46	12.4		162.68	180.70	125. 68	119				-
OS (h)	3.79	10.4		2.66	1.80	4.446	0.57	0.71	1.14	1.32	3 h min
SN	211.6	78.3	73.41	200.78	200.81	194.99	201				-
ρ at 15 °C (kg/m³)	891.9	893.9	891.5	886.50	889.60	891.5			884.4	886.1	
ρ at 20 °C (kg/m³)	888.2	889.7		-	885.90						
ρ at 25 °C (kg/m³)	884.5			-							860-900
ρ at 30 °C (kg/m³)	880.5			-							
ρ at 40 °C (kg/m³)	873.6			-			871	870.4	866.1	867.1	

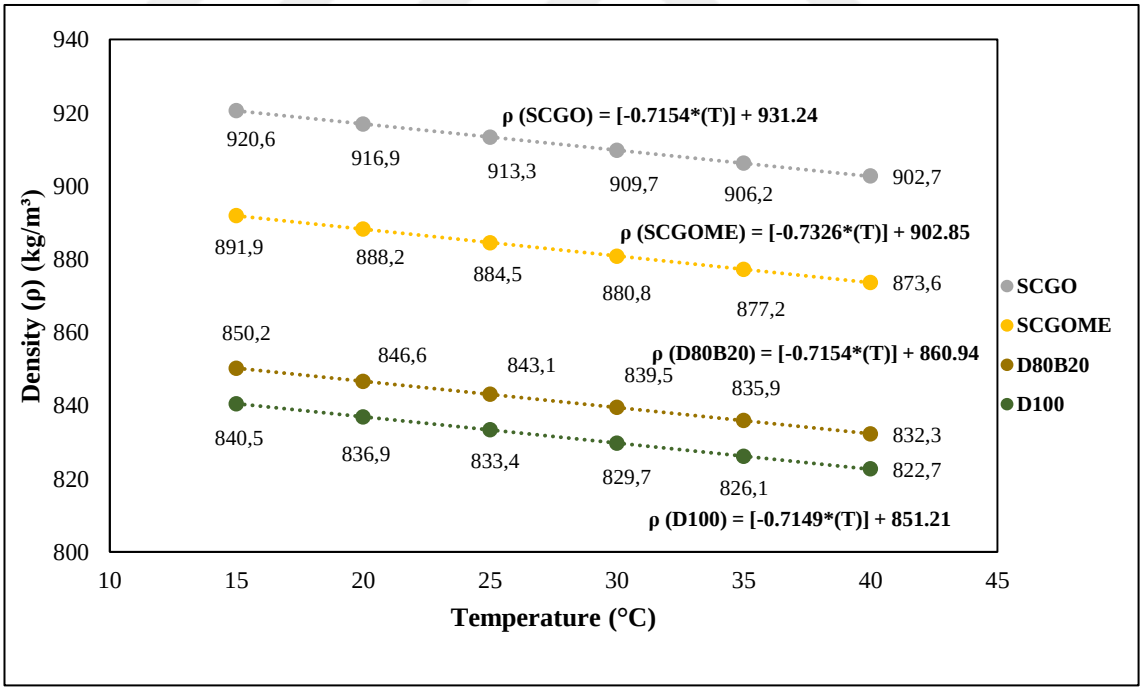
SME ≡ Safflower methyl ester, AMME ≡ *Aleurites moluccanus* oil methyl ester, HME ≡ Hemp methyl ester, PEME ≡ *Pangium edule* methyl ester, CMME ≡ *Croton megalocarpus* methyl ester, CPME ≡ *Ceipa pentandra* methyl ester, NSME ≡ *Nigella sativa* methyl ester.

Table 3.3. Properties of SCGOME-D100 binary blend and SCGOME-D100-But/Pen/Oct ternary blends

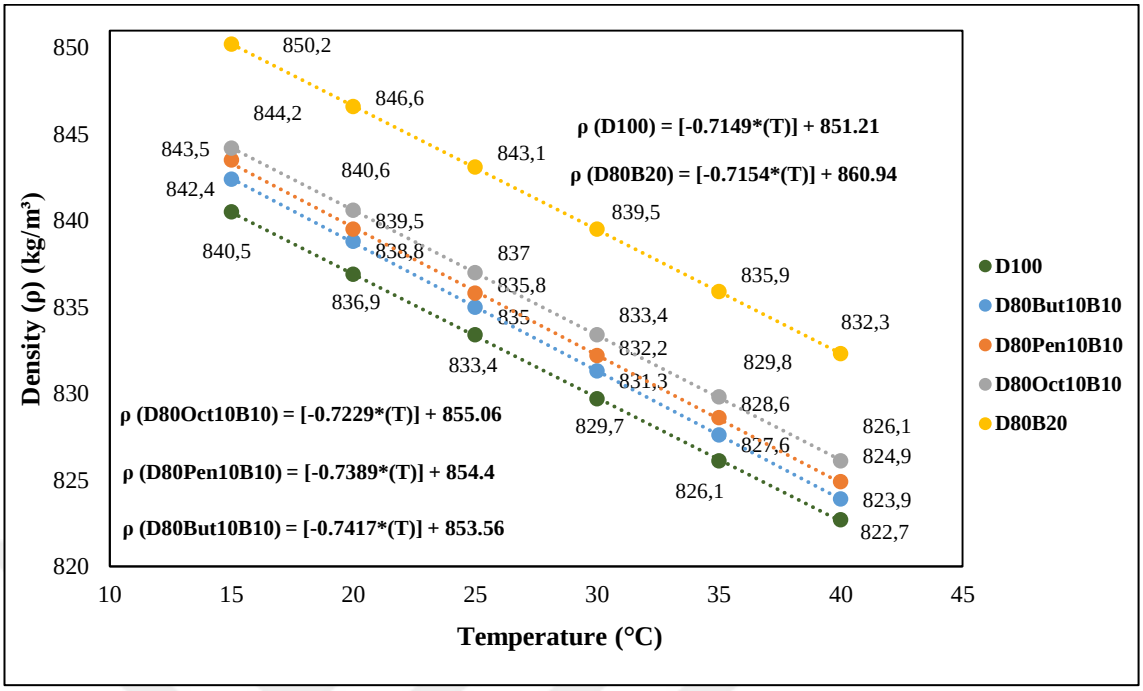
Property	**D80B10But10**	**D80B10Pen10**	**D80Oct10B10**	**D80B20**	**D100**	**But**	**Pen**	**Oct**
CP (°C)	-4	-3	-4	-3	-4			
PP (°C)	-15	-16	-14	-8	-24			
CFPP (°C)	-24	-21	-22	-16	-31			
FP (°C)	41.5	51.5	69.5	71	68.5			
ρ at 15 °C (kg/m³)	842.4	843.1	844.2	850.2	840.5	815.5	819.8	830.8

Table 3.4. Effect of temperature on density (ρ) of SCGO, SCGOME, But100, Pen100, Oct100, D100 and binary SCGOME-D100 and ternary SCGOME-D100-But/Pen/Oct blends

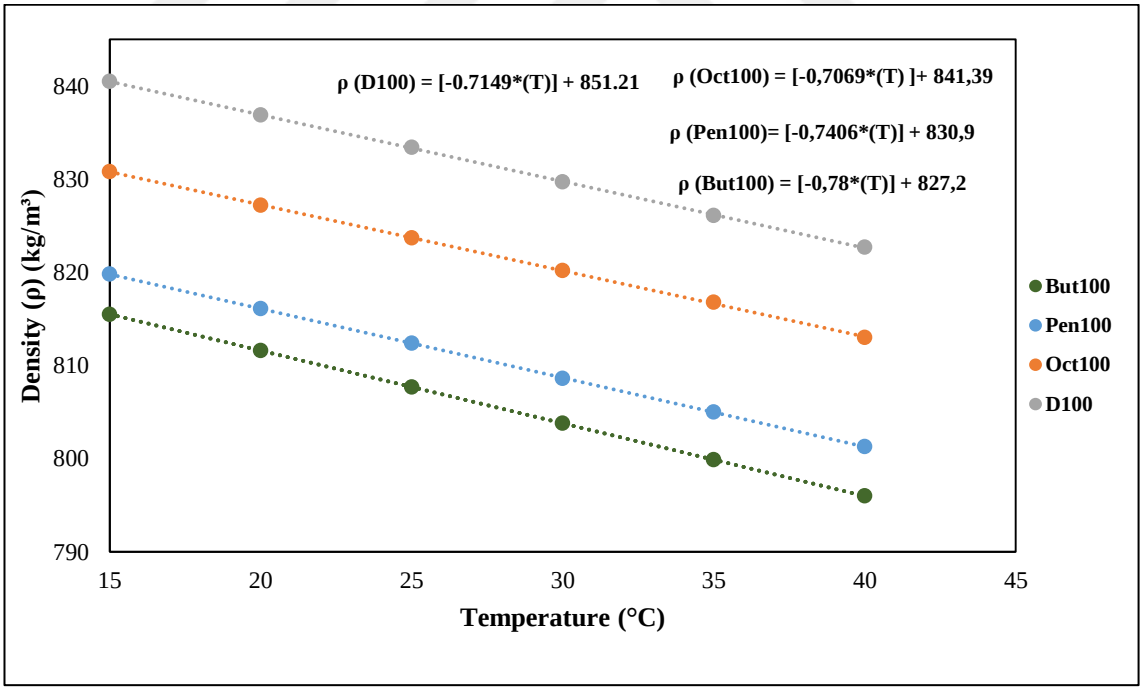
Type	Temperature (°C)					
	15	20	25	30	35	40
SCGO	920.6	916.9	913.3	909.7	906.2	902.7
SCGOME	891.9	888.2	884.5	880.8	877.2	873.6
D80But10B10	842.4	838.8	835	831.3	827.6	823.9
D80Pen10B10	843.5	839.5	835.8	832.2	828.6	824.9
D80Oct10B10	844.2	840.6	837	833.4	829.8	826.1
D80B20	850.2	846.6	843.1	839.5	835.9	832.3
D100	840.5	836.9	833.4	829.7	826.1	822.7
But100	815.5	811.6	807.7	803.8	799.9	796
Pen100	819.8	816.1	812.4	808.6	805	801.3
Oct100	830.8	827.2	823.7	820.2	816.8	813



(a) D100, SCGO, SCGOME and D80B20



(b) D100, D80But10B10, D80Pen10B10, D80Oct10B10 and D80B20



(c) D100, But100, Pen 100 and Oct100

Figure 3.1. Effect of temperature variations (15-40 °C) on density (ρ) of SCGO, SGOME, D100, D80B20, D80But10B10, D80Pen10B10, D80Oct10B10, But100, Pen 100 and Oct100

3.4. FAC, DU and LCSF of SCGOME

The FAC of biodiesel plays an important role in determining these properties. FAC depends on the nature of the feedstock, plant species, growth condition and the geographical location from where it was collected [5]. FAC profile of SCGOME was identified and listed in Table 3.5. Total saturated, monounsaturated and polyunsaturated, LCSF and DU of SCGOME were compared with those of SCGOME [102], spent coffee ground/waste cooking oil methyl ester (SCGOME/WCOME) [8], HME [31], SME [25] and AMME [30]. It can be seen that SCGOME has saturated, monounsaturated and polyunsaturated fatty acids of 10.24, 42.23 and 47.53% respectively. This has resulted in DU and LCSF of 141.54 and 6.94 in which the DU was higher than SCGOME (99.9) [102], SCGOME/WCOME (89.02) [8] and HME (128.55) [31] and lower than SME (163.40) [25] and AMME (180.38) [30]. SCGOME was basically dominated by linoleic acid (C18:02) (42.972%) followed by 14-Pentadecenoic acid (C15:01) (33.37%), stearic acid (C18:0) (8.758%), heptadecenoic acid (C17:01) (7.464%) and linolenic acid (C18:03) (4.1515%) accomplishing a FAC profile of 100% and proved that the final product was a 100% FAME. It is noteworthy to say that, DU has a direct impact on CN, OS and IV as the increase in DU reduces the OS and CN and increases the IV (Equations 4-6). Moreover, as per Equations 3 and 9, the increase in N (number of double bonds in each fatty acid) or DU due to the presence of mono and polyunsaturated fatty acids reduces the KV and the HHV respectively. All of which justifies the obtained properties in this study.

Table 3.5. FAC, DU and LCSF of SCGOME

Fatty acid	**MW_i**	**Structure**	**N**	**Chemical name**	**Formula**	**%FAME**
Butyric	88.11	C4:00	0	Butanoic acid	$C_4H_8O_2$	0.062
Caprylic	144.21	C8:00	0	Octanoic acid	$C_8H_{16}O_2$	0.075
Lauric	200.32	C12:00	0	Dodecanoic acid	$C_{12}H_{24}O_2$	0.338
Tridecylic	214.35	C13:00	0	Tridecanoic acid	$C_{13}H_{26}O_2$	0.073
Pentadecylic	242.40	C15:00	0	Pentadecanoic acid	$C_{15}H_{30}O_2$	0.160
14-Pentadecenoic acid	240.38	C15:01	1	Pentadec-14-enoic acid	$C_{15}H_{28}O_2$	33.37
Palmitoleic	254.41	C16:01	1	Hexadec-9-enoic acid	$C_{16}H_{30}O_2$	0.1333
Heptadecenoic	268.44	C17:01	1	2-heptadecylenic acid	$C_{17}H_{32}O_2$	7.464
Stearic	284.48	C18:00	0	Octadecanoic acid	$C_{18}H_{36}O_2$	8.758
Oleic	282.47	C18:01	1	Cis-9-Octadecenoic	$C_{18}H_{34}O_2$	0.571
Linoleic	280.44	C18:02	2	Cis-9-cis-12 Octadecadienoic	$C_{18}H_{32}O_2$	42.972
Linolenic	278.43	C18:03	3	Alpha-Linolenic acid	$C18H_{30}O_2$	4.1515
Arachidic	312.53	C20:00	0	Eicosanoic	$C_{20}H_{40}O_2$	0.3525
Paullinic	310.52	C20:01	1	Cis-13-eicosenoic acid	$C_{20}H_{38}O_2$	0.5861
Eicosadienoic	308.56	C20:02	2	Cis-11,14-Eicosadienoic acid	$C_{20}H_{36}O_2$	0.311
Eicosatrienoic	306.48	C20:03	3	Eicosatrienoic acid	$C_{20}H_{34}O_2$	0.0960
Heneicosanoic	326.56	C21:00	0	Heneicosanoic acid	$C_{21}H_{42}O_2$	0.184
Erucic	338.57	C22:01	1	(Z)-Docos-13-enoic acid	$C_{22}H_{42}O_2$	0.0998
Lignoceric	368.64	C24:00	0	Tetracosanoic acid	$C_{24}H_{48}O_2$	0.239
Total						**100**

N ≡ Number of double bonds, MW_i ≡ Molecular weight of fatty acid.

	SCGOME	SCGOME [102]	SCGOME/WCOME [8]	HME [31]	SME [25]	AMME [30]
Saturated	10.24	45.2	41.0	30.82	8.95	9.71
Monounsaturated	42.23	12.7	29.98	10.40	18.69	25.12
Polyunsaturated	47.53	39.8	29.02	58.78	72.36	65.17
Total	100	100	100	100	100	100
DU	141.54	99.9	89.02	128.55	163.40	180.38
LCSF	6.94	23. 65	26.42	22.35	5.82	6.31

	SCGOME [50]
Saturated	48.9
Monounsaturated	7.2
Polyunsaturated	23.3
Total	79.44
DU	53.8
LCSF	23.65

3.5. NMR analyses

NMR analyses for fuel samples were performed using Bruker 400 NMR at 400 MHz (^{1}H) and 100 MHz (^{13}C) with the residual solvent peaks as internal references. A spectrometer equipped with suitable probes for cores of ^{1}H, ^{13}C, ^{19}F, ^{31}P. $CdCl_3$ was used as both the solvent as well as internal standard respectively. ^{1}H and ^{13}C spectra were recorded.

3.5.1. ^{13}C NMR analysis

In this study, SCGO and its methyl ester (SCGOME), But100, Oct100, Pen, D100 and their ternary blends (D80But10B10, D80Oct10B10, D80Pen10B10) were characterized by C-NMR spectroscopy and their representative spectrum of $^{13}CNMR$ are shown in Figs. 3.2 and 3.3, which shows the characteristic peaks of ester and carbonyl δ (-COO-) and δ (-C=O-) at around 100 and 0 ppm, respectively. The peaks at around 14 ppm are due to the terminal carbon of methyl groups δ ($-CH_3$) and signals at 10–35 ppm are related to methylene carbons δ ($-CH_2-$) of long carbon chain in FAMEs [104].

3.5.2. ^{1}H NMR analysis

In this study, SCGO and its methyl ester (SCGOME), But100, Oct100, Pen100, D100 and their ternary blends (D80But10B10, D80Oct10B10, D80Pen10B10) were characterized by H-NMR spectroscopy and their spectra are shown in Figs. 3.4 and Figure 3.5. The characteristic peaks of methoxy protons δ($-O-CH_3$) were observed as a singlet at around 3.65, 3.68, 3,69, 3,69 and 3.71 ppm for SCGOME, D80But10B10, D80Oct10B10, D80Pen10B10 and B20D80, respectively. These chemical shifts indicate the presence of methyl esters in biodiesel. Other observed peaks were around between 0.86 and 0.95 ppm of the terminal methyl δ ($-CH_3$) protons [105].

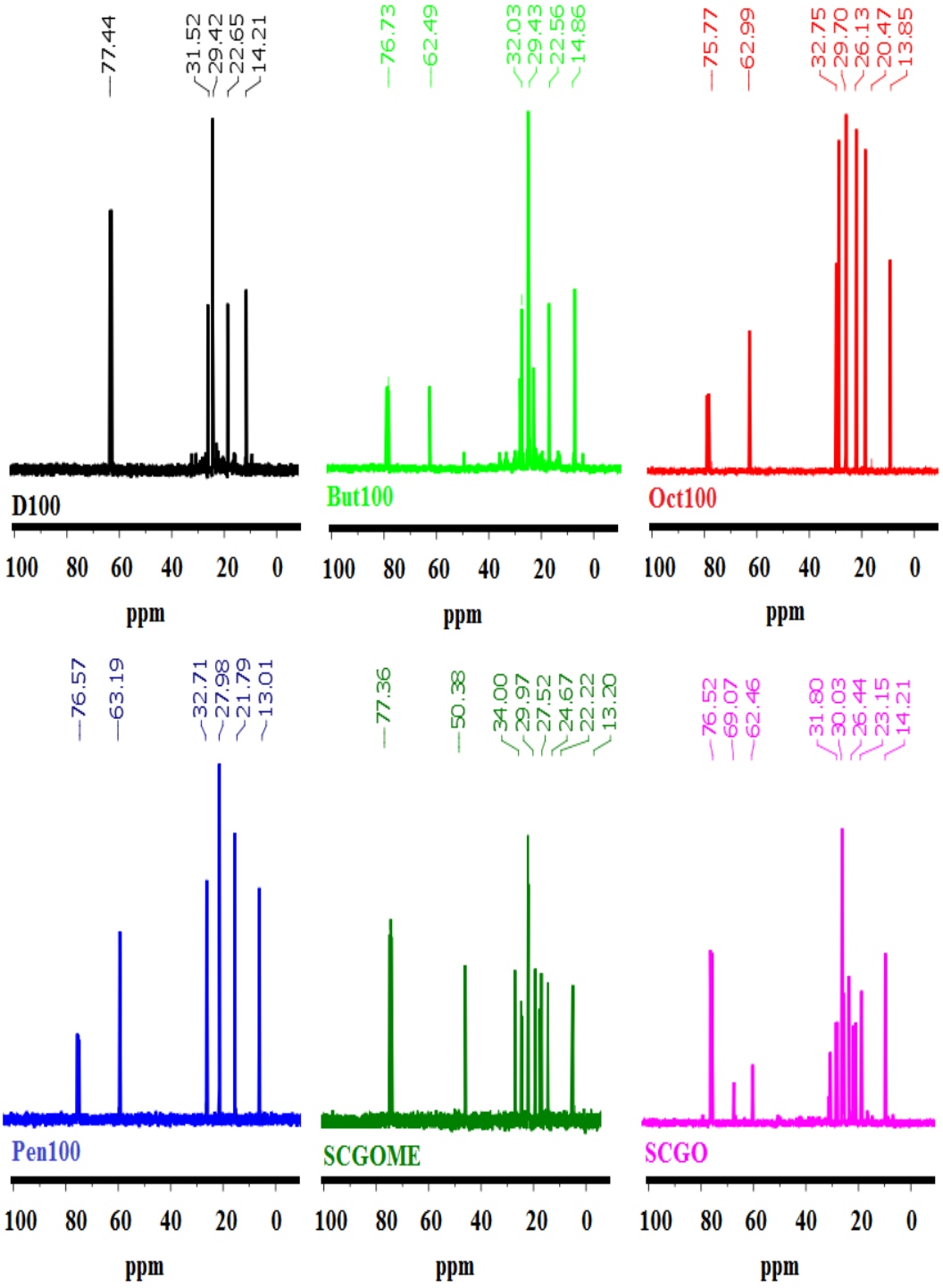


Figure 3.2. C-NMR spectra of D100, But100, Oct100, Pen100, SCGO and SCGOME

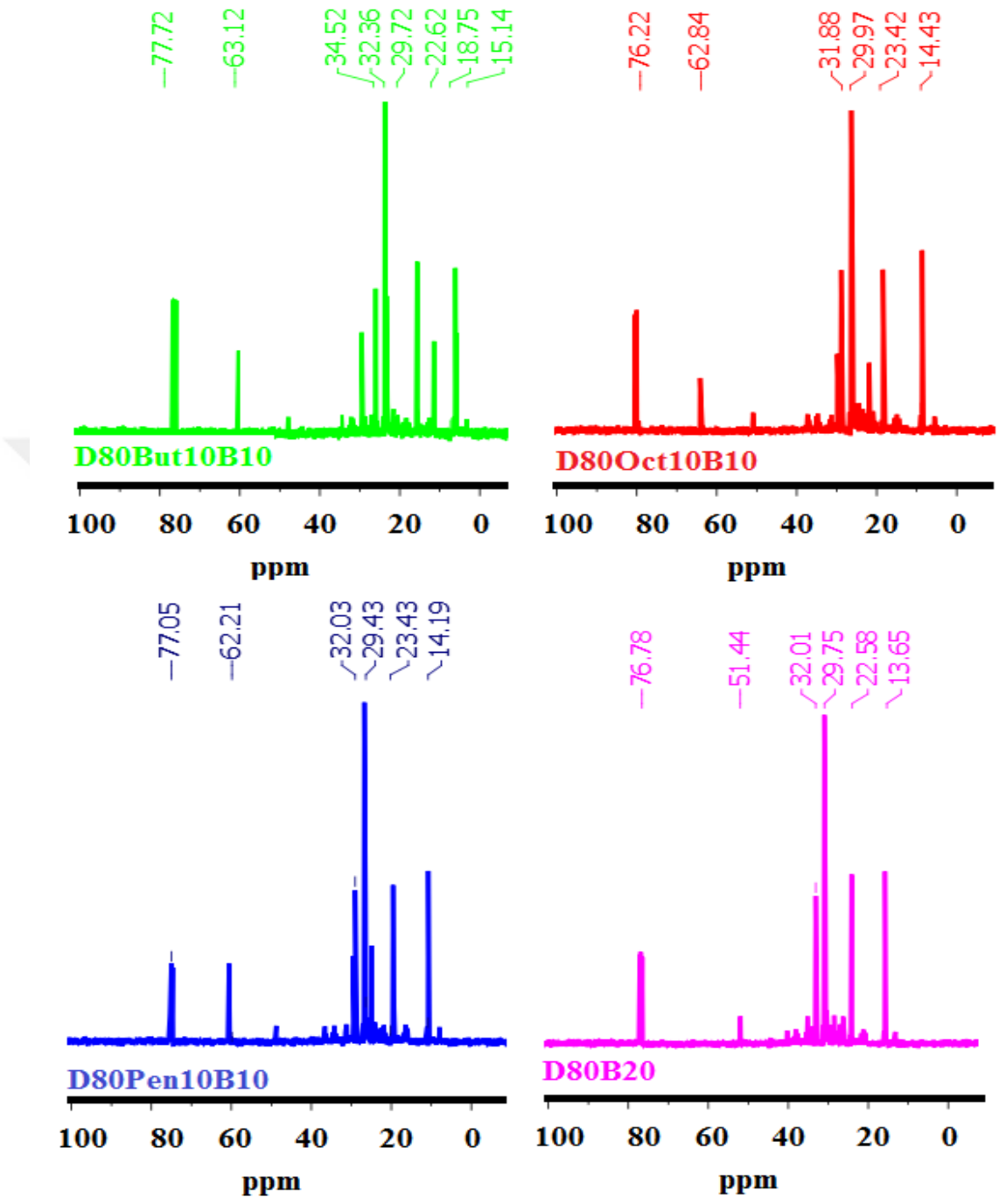


Figure 3.3. C-NMR spectra of D80But10B10, D80Oct10B10, D80Pen10B10 and B20BD80

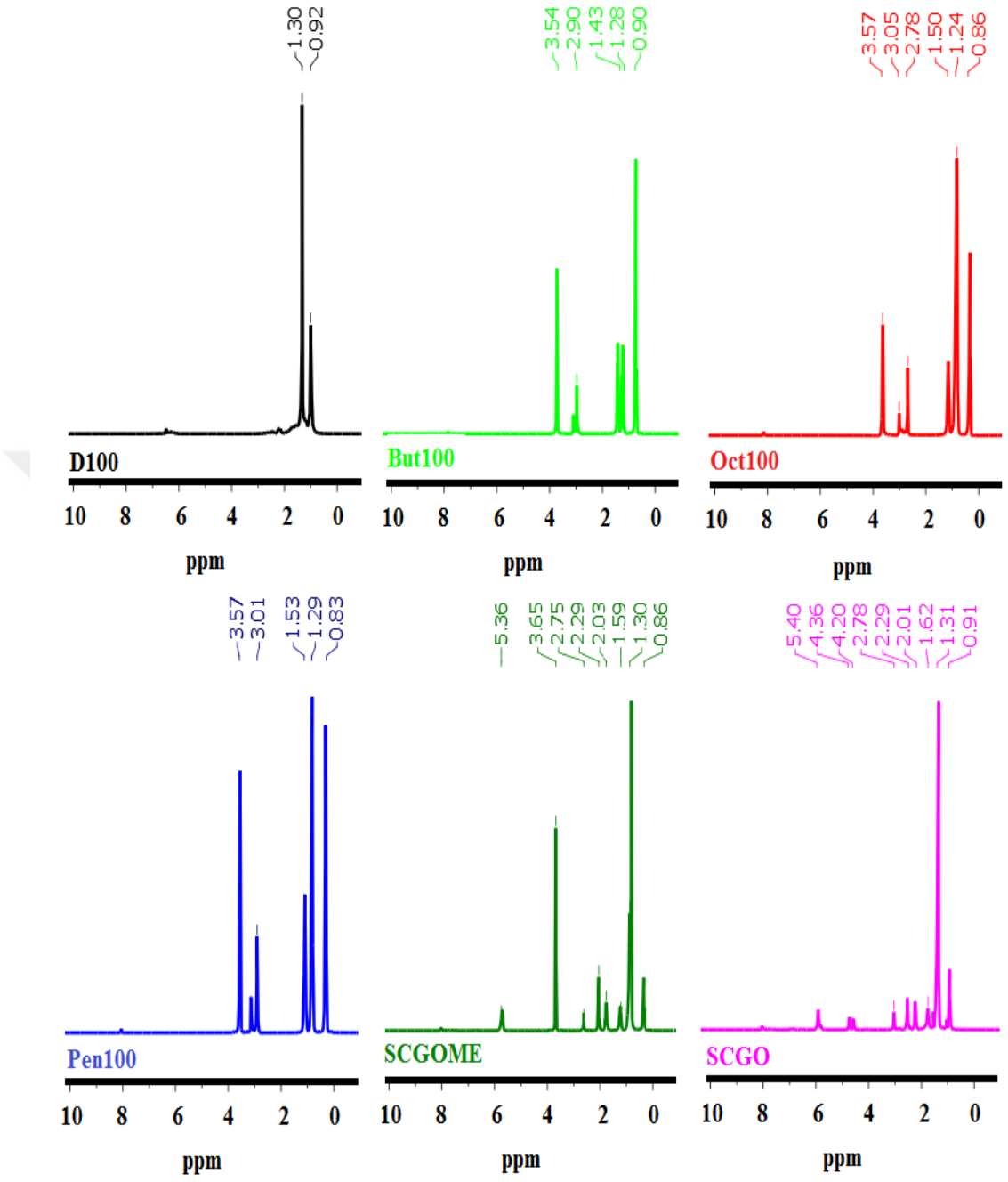


Figure 3.4. H-NMR spectra of D100, But100, Oct100, Pen100, SCGO and SCGOME

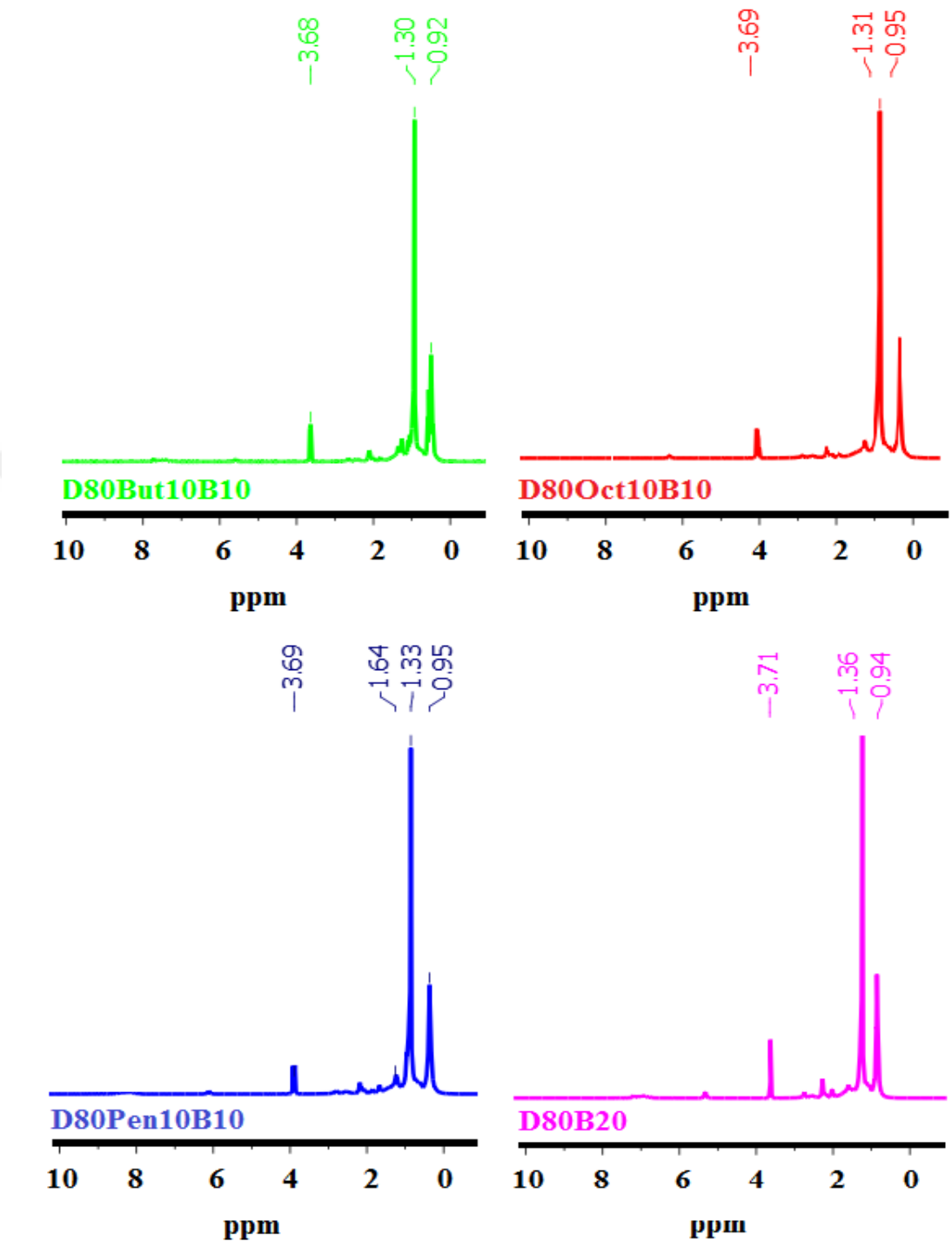


Figure 3.5. H-NMR spectra of D80But10B10, D80Oct10B10, D80Pen10B10 and B20D80

3.6. FT-IR analysis

Oils and ester groups have strong absorbance forces in the infrared region [106]. Recently, the addition of biodiesel as well as higher alcohols to fossil diesel in order to improve the properties of fuels used in diesel engines has been investigated. An excess of carbon numbers in the carbon chain of alcohols containing alkyl and hydroxyl groups allows the alcohols to be easily mixed with organic compounds. Thus, biodiesel samples can be easily mixed with alcohols that have more carbon than alcohols with less carbon. Alcohol-added fuels are called oxygenated fuel.

In this study, SCGOME and its blends with D100, But100, Oct100 and Pen100 were analyzed to determine the existence of methyl ester and alcohols functionals by FT-IR spectra. Figure 3.6 displays the infrared spectra of D100, But100, Oct100, Pen100, SCGO and SCGOME while Figure 3.7 displays the infrared spectra of D20But10B10, D20Oct10B10, D20Pen10B10 and D20B80. The lists of functional groups and types of vibration were shown in Table 3.6. It can be seen clearly from Figure 3.6 and Figure 3.7, that a strong absorption of FAME exists at nearly 1745 cm^{-1}. The characteristic absorption bands for –OH groups in alcohols occurs nearly between 3300-3500 cm^{-1}. It can be seen that Figure 3.6 and Figure 3.7, the intensities of the absorbance decreased as the number of carbons increased with addition of different higher alcohols into diesel-biodiesel samples. The presence of the =C-H and $-(CH_2)_n$ methylene groups of cis disubstituted alkenes and aromatic can be seen at nearly 722 cm^{-1}. The presence of C-O of alkoxy esters can be seen at nearly1240-1030 cm^{-1} in samples. The intensities of peaks at 2920 cm^{-1} and 2859 cm^{-1} are attributed to C-H of alkanes and methylenes in D100.

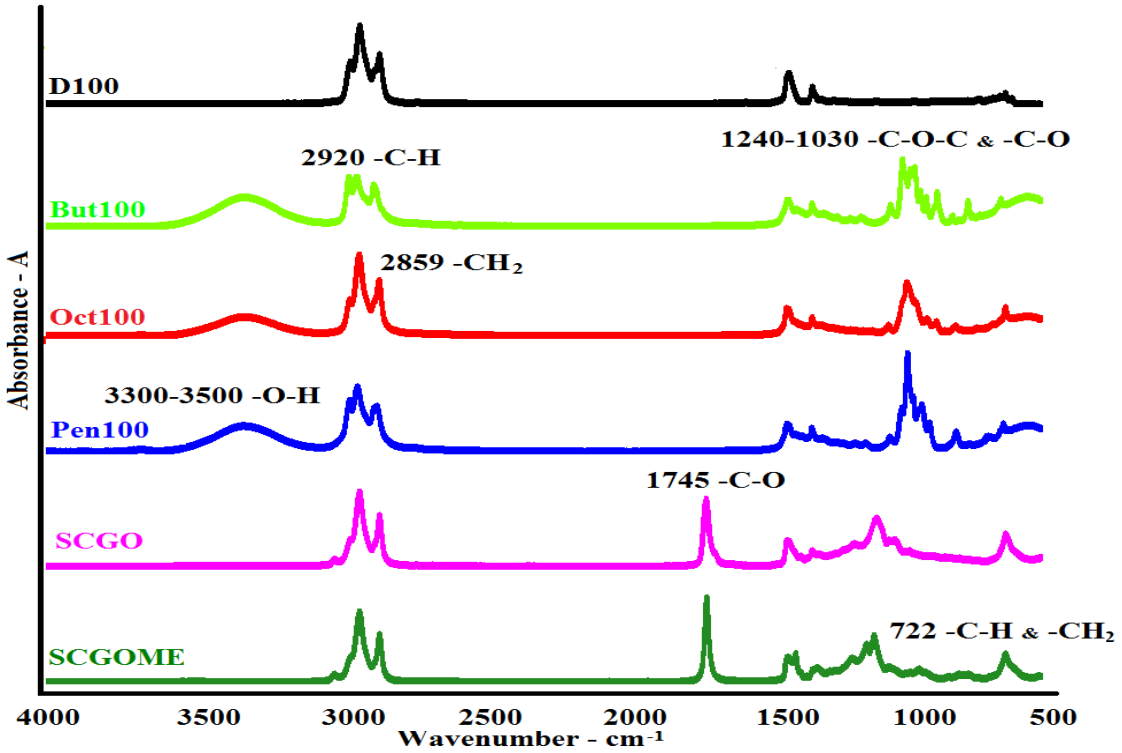


Figure 3.6. Infrared spectra of D100, But100, Oct100, Pen100, SCGO and SCGOME

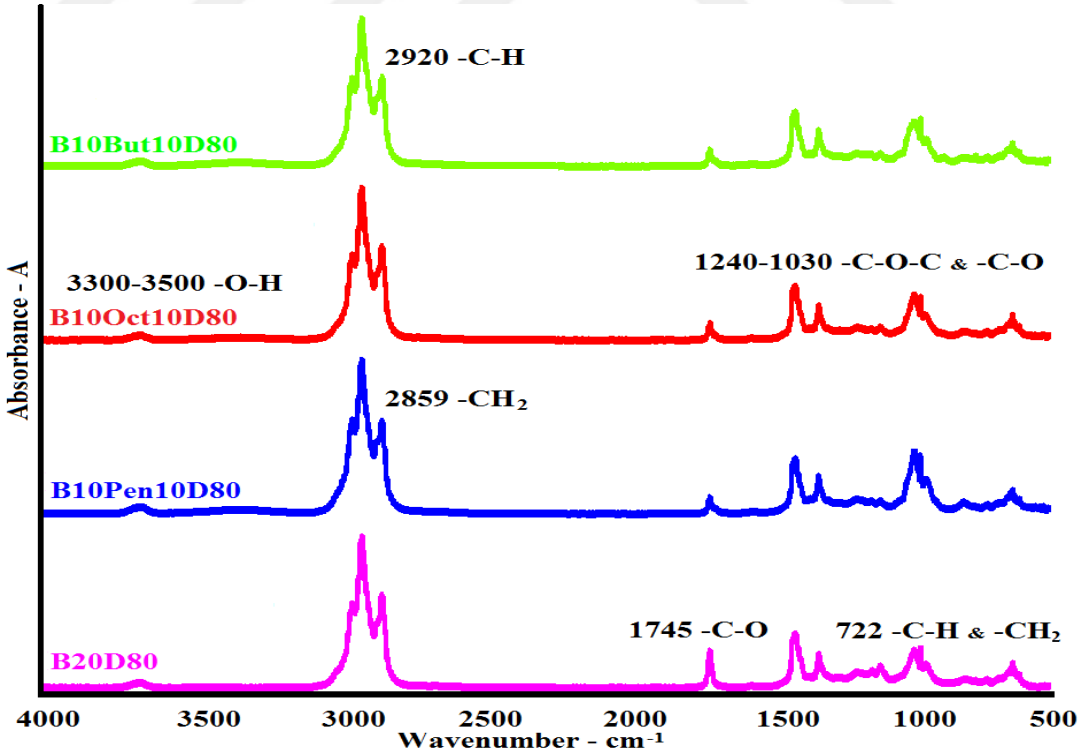


Figure 3.7. Infrared spectra of D20But10B10, D20Oct10B10, D20Pen10B10 and D20B80

Table 3.6. Functional group frequencies of D100, But100, Oct100, Pen100, SCGO, SCGOME and their blend [8]

Wavenumber, cm^{-1}	Functional groups and types of vibration
3300-3500	O-H of alcohols - Stretching
2920	C-H of alkanes - Asymmetrical stretching
2589	C-H of methylenes - Symmetrical stretching
1745	C=O of esters - Stretching
1240-1030	C-O of alkoxy esters - Stretching
722	=C-H and -(CH_2)n methylene groups of cis disubstituted alkenes and aromatic - Bending

3.7 UV-Vis analysis

Figure 3.8. shows a typical family of absorbance curves for SCGOME, D80B20, D80But10B10, D80Oct10B10, D80Pen10B10 in the range of 400 to 200 nm. Analysis of absorbance curves for SCGOME and its blends showed that a single wavelength in the UV range could be used to determine the blend level for a single diesel fuel [107]. The absorbance decreased linearly with increasing concentration of blend (Figure 3.8). When percent biodiesel was plotted against absorbance for any given wavelength between 290 and 300 nm and a linear relation was observed for blends of SCGOME. This was attributed to the decreasing concentration of aromatic compounds in the fuel.

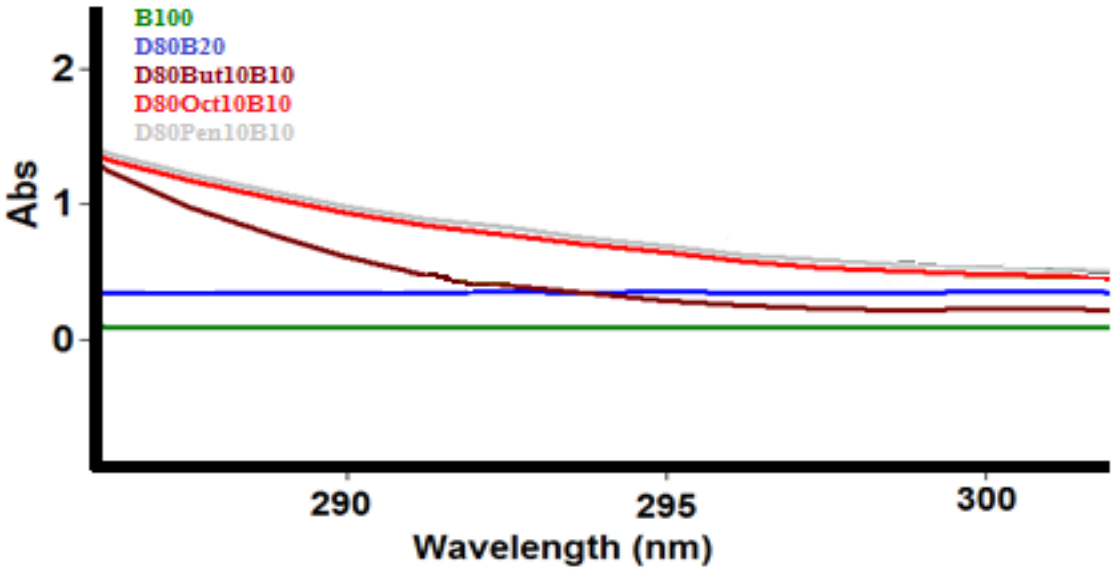


Figure 3.8. UV absorbance spectra of SCGOME, B20D80 D80But10B10, D80Oct10B10 and D80Pen10B10

3.8. TGA analysis

Thermal stability of the SCGOME and their blends with diesel and alcohols (But100, Oct100 and Pen100) were studied by thermogravimetric analyses (TGA) in the temperature range of 25–700 ^{o}C, under air stable condition and their respective thermograms are shown in Figure 3.9. This TGA analysis technique is utilized for the characterizing thermal as well as oxidative stability of a compound or mixture by measuring the changes in its physico–chemical properties. These properties were expressed as weight or mass change (in g or %) as a function of increasing temperature (in ^{o}C). From the thermograms (TGA or DrTGA) curves (Figs. 3.9 and 3.10) clearly shown that the oxidative degradation occurred in a single continuous step in the temperature range 25–300 °C for SCGOME and their blends. In these temperature ranges, the mass losses occur at levels of 94.4–99.4% for spent SCGOME blends. The thermal degradation But100, Oct100, Pen100 and D100 occurred at 33.10, 59.70, 43.00 and 72.90 °C respectively. Moreover, in these temperature range, the percentage of mass losses occurred at 99.05 % and 97.84 % and also, their thermal onset temperatures were represented in Table 3.7. It can be seen that the onset temperature for the blends changes depending on the type of alcohol.

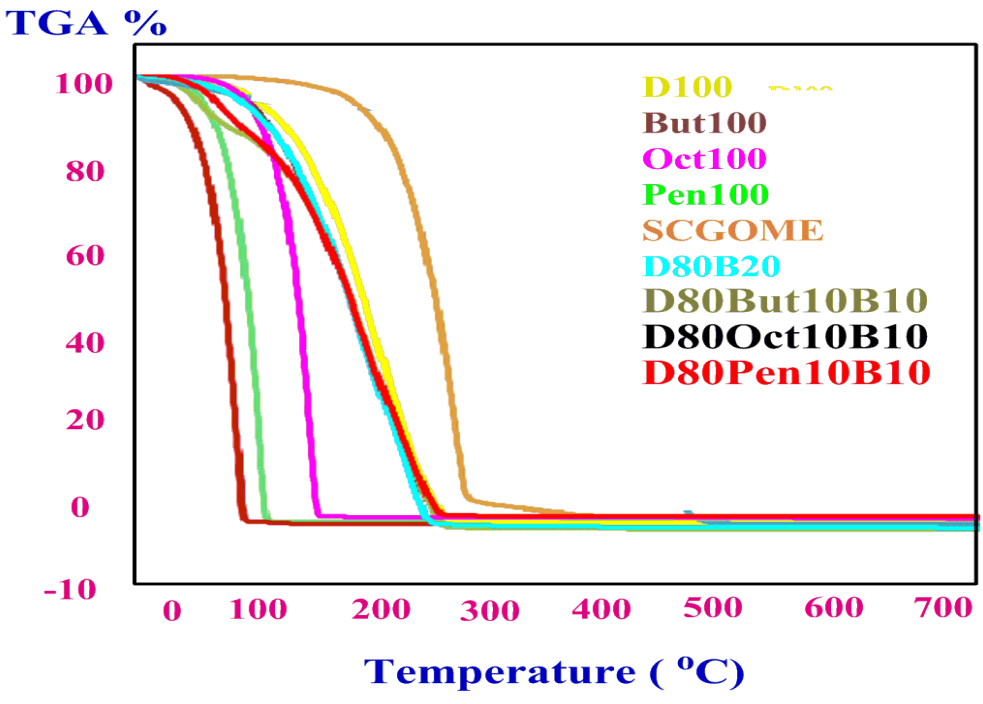


Figure 3.9. TGA of SCGOME, D100 and their blends with But, Pen and Oct for thermal stability

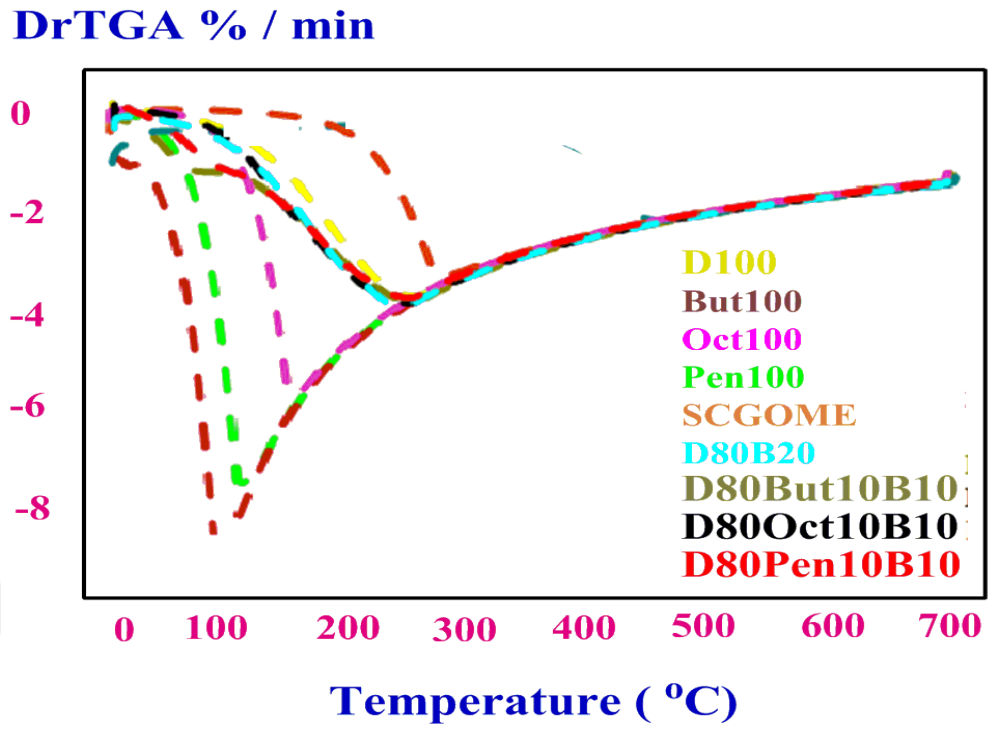


Figure 3.10. Derivative thermogravimetric analyses (DrTGA) of SCGOME, D100 and their blends with But, Pen and Oct for thermal stability

Table 3.7. TGA of SCGOME, But100, Oct100, Pen100, D100, D80B20, D80But10B10, D80Oct10B10 and D80Pen10B10

Sample name	Heating rate (°C/min)	Temperature Ranges (°C)	Onset temperature for thermal degradation (°C)	Mass loss under dry air (%)
D100	10	25–264	33.10	99.00
SCGOME	10	25–283	113.10	94.84
But100	10	25–104	33.10	99.05
Oct100	10	25–162	59.70	97.84
Pen100	10	25–122	43.00	98.60
D80B20	10	25–249	50.70	99.24
D80But10B10	10	25–258	50.10	99.47
D80Oct10B10	10	25–257	63.10	98.80
D80Pen10B10	10	25–258	44.90	97.50

3.9. DSC analysis

The crystallization onset temperatures of SCGO and its methyl ester (SCGOME) besides But100, Oct100, Pen100, D100 and their blends (B20D80, D80But10B10,

D80Oct10B10, D80Pen10B10) were experimentally tested using DSC and the results are presented in Table 3.8. The crystallization onset temperatures for SCGO, SCGOME, But100, Oct100, Pen100, and D100 are -3.36 °C, -0.54 °C, -109.51 °C, -22.22 °C, -110.18 °C and -8.57 °C respectively. Hence, biodiesel crystallizes faster than D100, But, Pen and Oct [31]. On the other hand, the crystallization onset temperatures of B10But10D80, B10Oct10D80, B10Pen10D80, and B20D80 are -7.03 °C, -7.31 °C, -6.64 °C and -6.91 °C respectively, below SCGOME implying that the addition of D100, But, Pen and Oct lowers the crystallization temperature of biodiesel [105]. The crystallization onset temperatures of SCGOME is in good agreement with -1.43 °C for SCGOME/WCOME [8], higher than -5.27 °C for HME [31], -7.42 °C for SME [25] and -9.96 °C [30] for AMME and lower than 17.07 °C for *Moringa oleifera* methyl ester (MOME) [108].

Table 3.8. Crystallization onset temperatures of SCGO, SCGOME, But100, Oct100, Pen100, D100 and their binary and ternary blends

Sample	**Crystallizations onset temperature (°C)**
SCGO	-3.36
SCGOME	-0.54
But100	-109.51
Oct100	-22.22
Pen100	-110.18
D100	-8.57
B20D80	-6.91
B10But10D80	-7.03
B10Oct10D80	-7.31
B10Pen10D80	-6.64

Table 3.9 conduct a quick comparison of crystallization onset temperatures of But100, Oct100 and Pen100 and compare with those of [8, 25, 31, 109] They explained that they could not detect it because BUT crystallization point was out of temperature range.

Table 3.9. Comparison of crystallization onset temperatures of But100, Oct100 and Pen100

Alcohol type	Crystallizations onset temperature (°C)	Reference
But	-15.13	**[8]**
But	-15.13	**[31]**
But	Not detected (between -70, +20)	**[109]**
But	-15.13	**[25]**
Pen	-18.09	**[8]**
But	-109.51	This study
Pen	-110.18	This study
Oct	-22.22	This study

3.10. Engine performance analyses

As indicated earlier, engine performance is affected by type of fuel and its properties. The following section discuss the obtained results for BSFC, average fuel consumption (AFC) and brake thermal efficiency (η_{bth}) of D100, B20D80, B10But10D80, B10Pen10D80 and B10Oct10D80 respectively.

3.10.1. BSFC

Figure 3.11 illustrates the results of BSFC of D100, B20D80, B10But10D80, B10Pen10D80 and B10Oct10D80 respectively at different loads and constant engine speed of 1800 rpm. It can be seen that BSFC decreases with increasing load. The maximum BSFC was recorded for D80Pen10B10 at 7.5 N.m load (525.48 kg/kwh) while the lowest BSFC was also recorded for D80Pen10B10 at 16 N.m (331.88.94 kg/kwh).

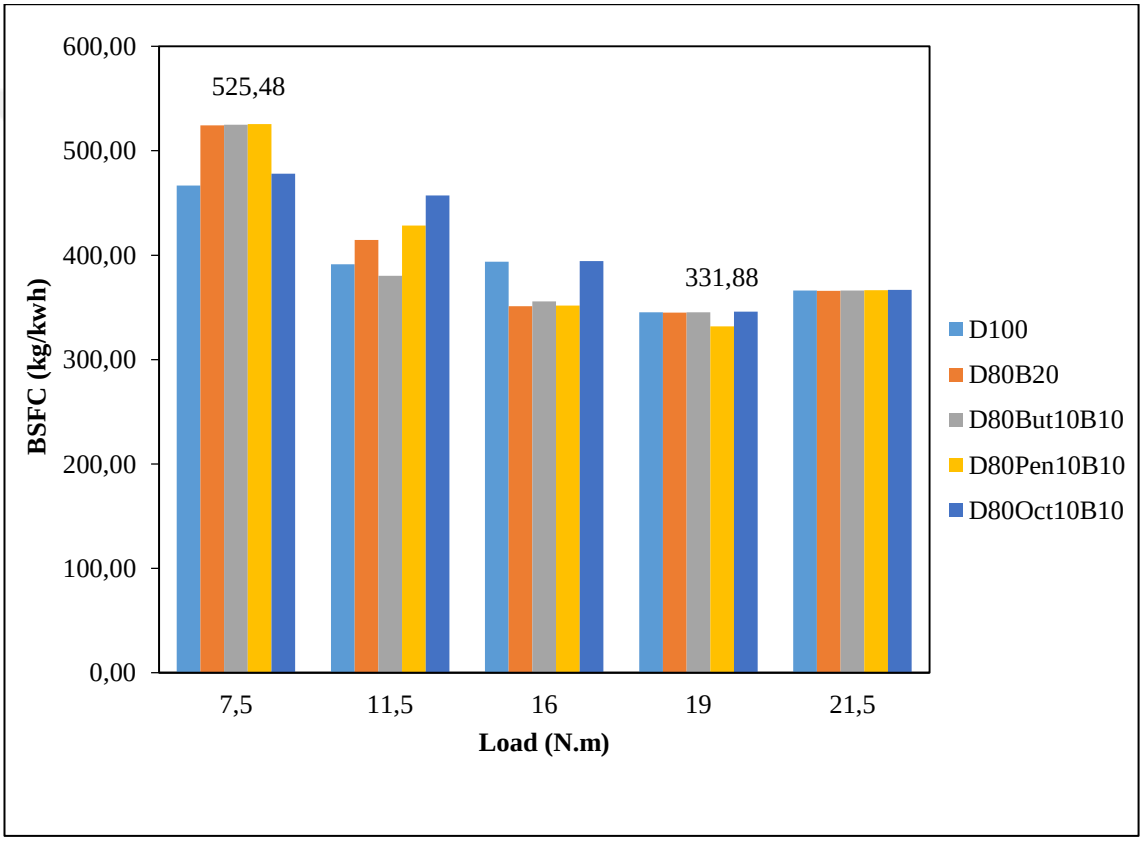


Figure 3.11. BSFC of all fuel samples at constant speed of 1800 rpm and different loads

3.10.2 AFC

Figure 3.12 illustrates the results of AFC of D100, B20D80, B10But10D80, B10Pen10D80 and B10Oct10D80, respectively at different loads and constant engine speed of 1800 rpm. It can be seen that AFC increase with increasing load for almost all tested fuels at the same speed. The maximum AFC was recorded for D80Oct10B10 at 21.5 N.m load (0.413 kg/s) while the lowest AFC was recorded for D100 at 0 N.m (0.127 kg/s).

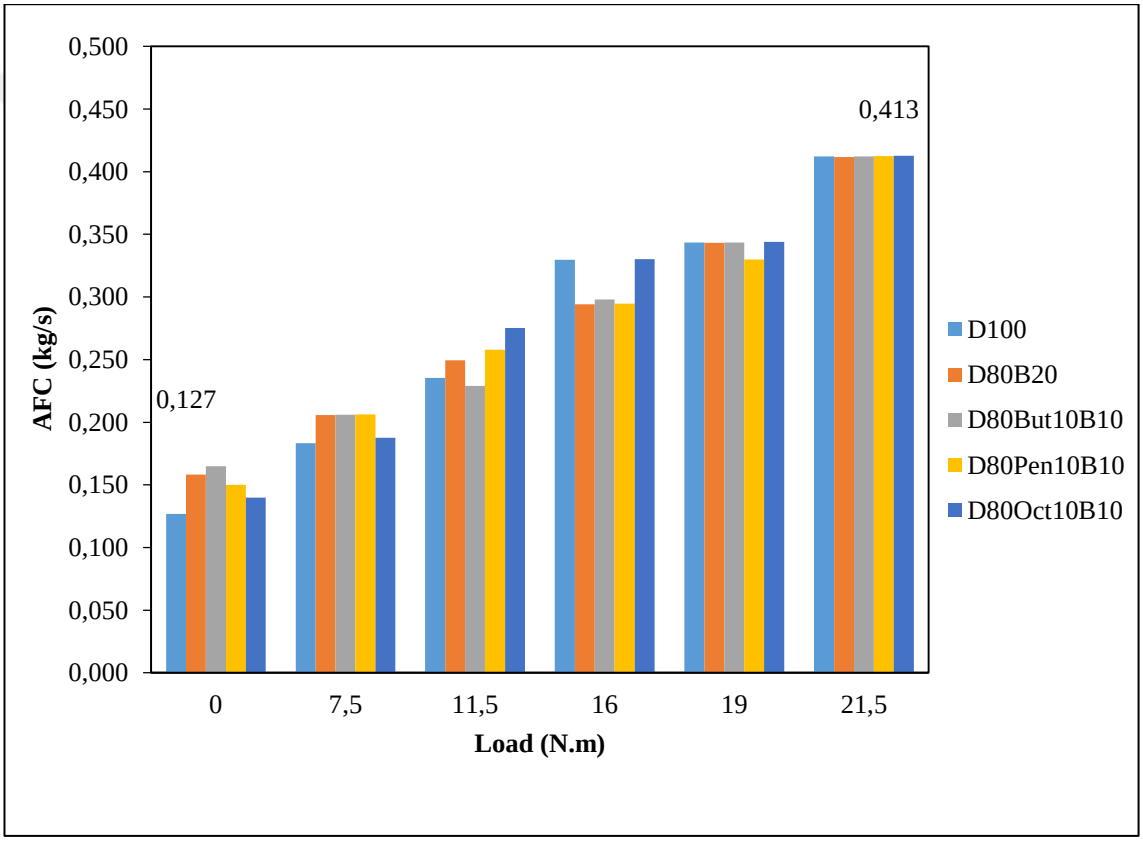


Figure 3.12. AFC for all fuel samples at constant speed of 1800 rpm and different loads

3.10.3 η_{bth}

Figure 3.13 illustrates the results of η_{bth} of D100, B20D80, B10But10D100, B10Pen10D80 and B10Oct10D80 respectively at different loads and constant engine speed of 1800 rpm. It can be seen (η_{bth}) increase when the load increased from 0 N.m to 19 N.m and then reduced again and again when the load increased to 21.5 The maximum η_{bth} was recorded for D80Pen10B10 at 19 N.m load (26.35 %) while the lowest η_{bth} was recorded for D80B20 at 0 N.m (16.58 %).

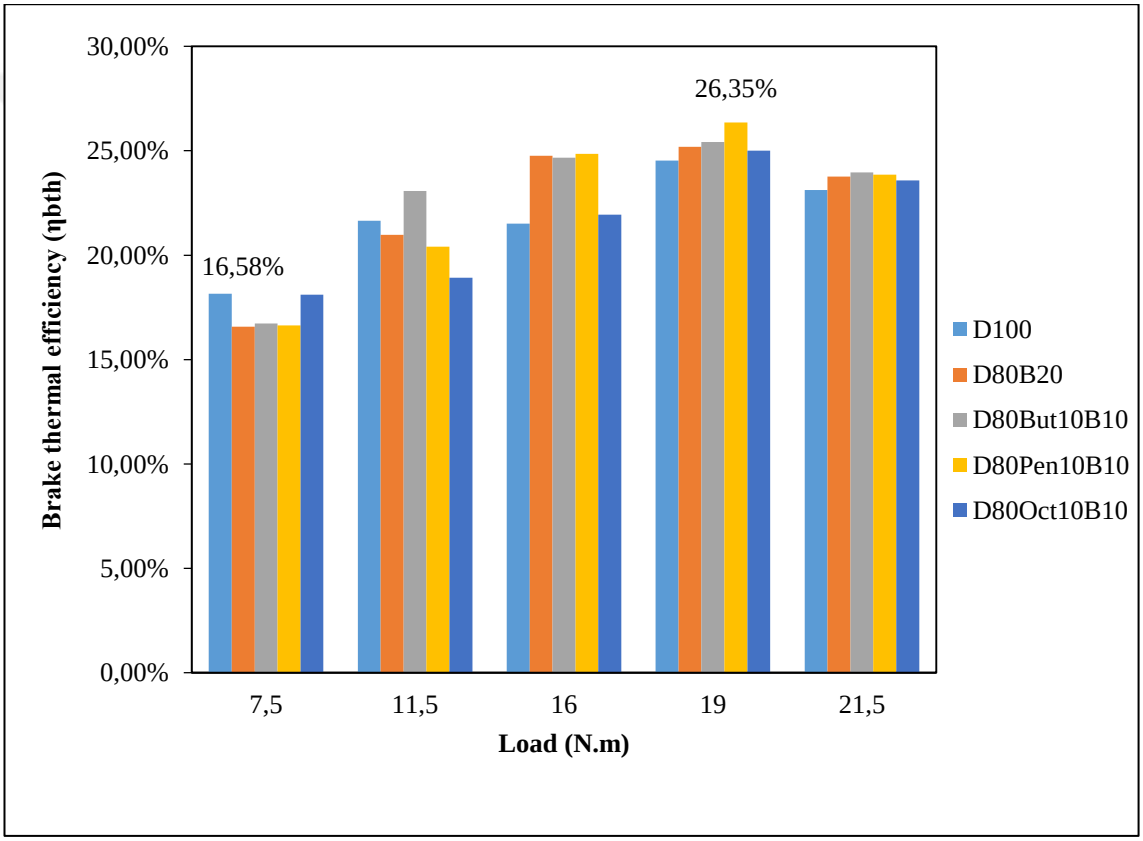


Figure 3.13. η_{th} for all fuel samples at constant speed of 1800 rpm and different loads

3.11. Emissions analyses

3.11.1. CO emissions

Figure 3.14 illustrates the variation of CO emissions results of D100, B20D80, B10But10D10 B10Pen10D80 and B10Oct10D80, respectively at different loads and constant engine speed of 1800 rpm. The maximum CO emissions was recorded for D80But10B10 at 7.5 N.m load (0.09 % vol) while the lowest recorded CO was recorded for D100 at 7.5 N.m (0.002 % vol).

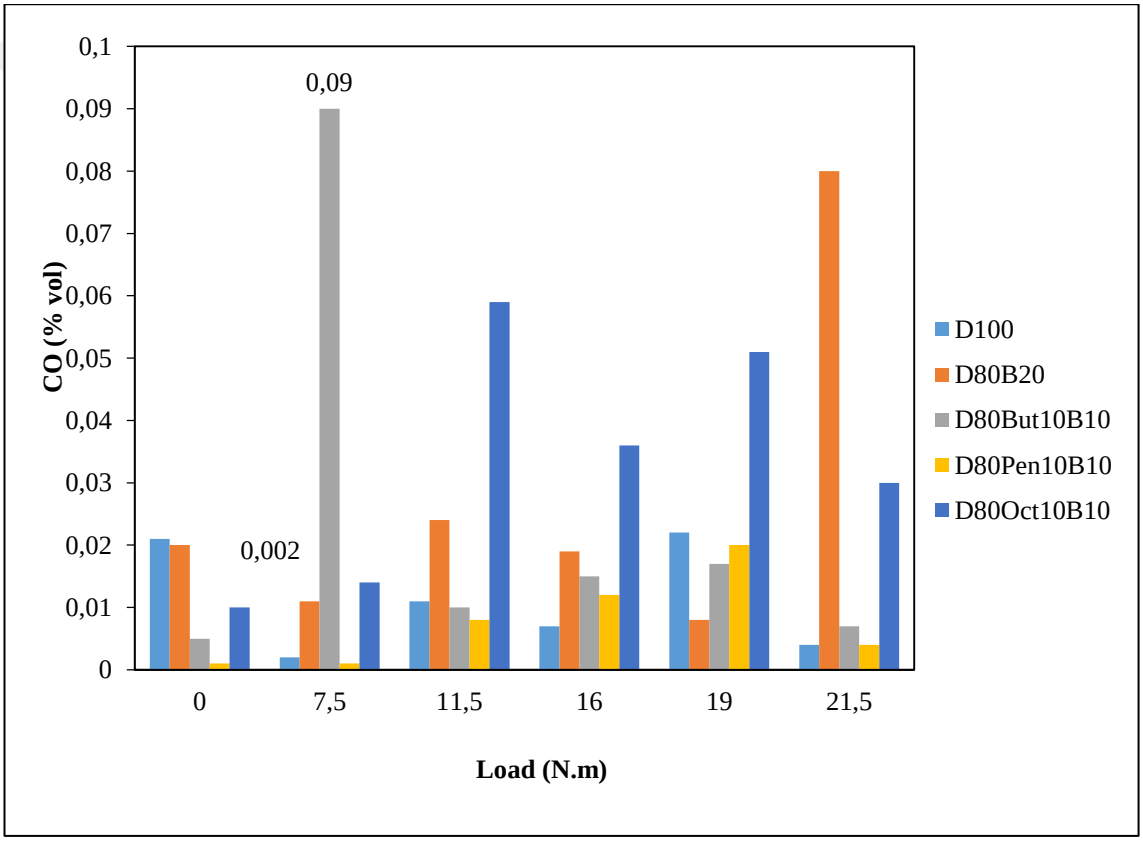


Figure 3.14. CO emissions for all fuel samples at constant speed of 1800 rpm and different loads

3.11.2. CO_2 emissions

Figure 3.15 illustrates the variation of CO_2 emissions results of D100, B20D80, B10But10D80, B15Oct15D70, B10Pen10D80 and B10Oct10D80, respectively at different loads and constant engine speed of 1800 rpm. The maximum CO_2 emissions was recorded for D80Oct10B10 at 19 N.m load (0.91 % vol) while the lowest recorded CO_2 was recorded for D100 and D80But10B10 at 11.5 and 16 N.m (0.3 % vol) respectively.

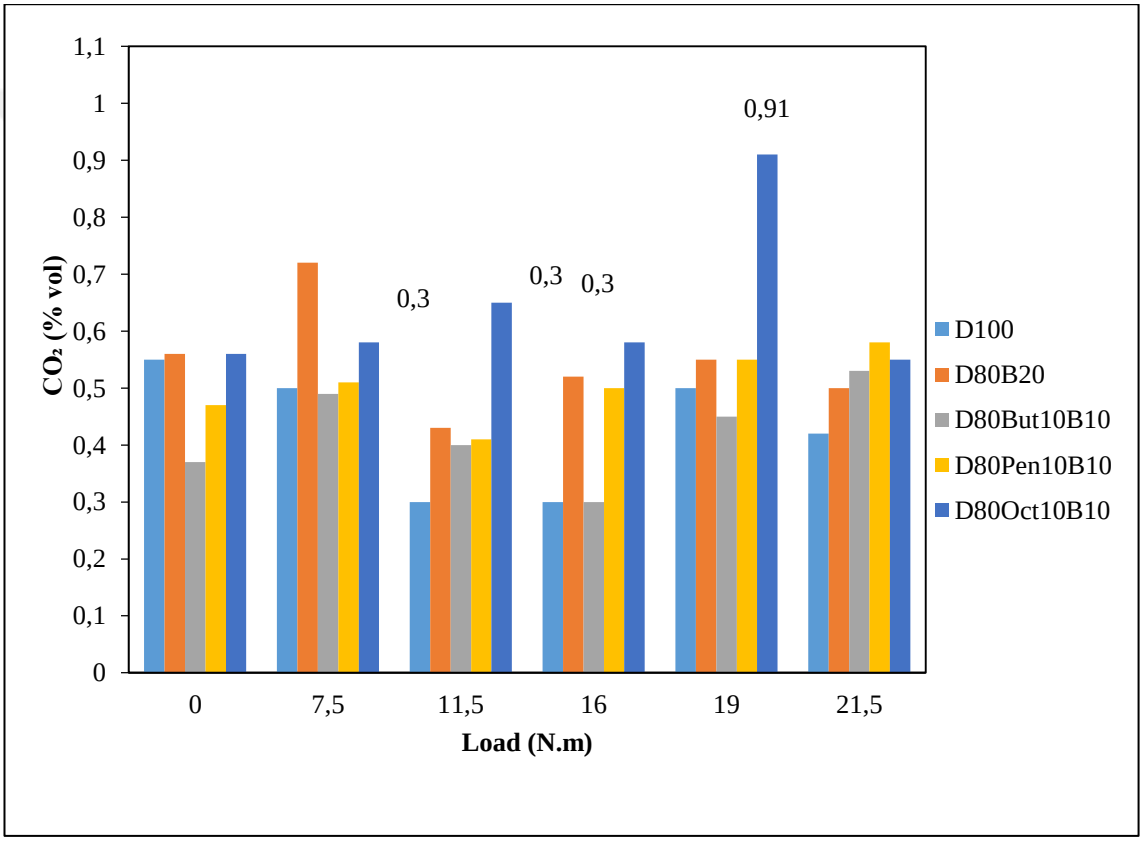


Figure 3.15. CO_2 emissions for all fuel samples at constant speed of 1800 rpm and n different loads

3.11.3 HC emissions

Figure 3.16 illustrates the variation of HC emissions results of D100, B20D80, B10But10D80, B10Pen10D80 and B10Oct10D80, respectively at no loads and constant engine speed of 1800 rpm. The maximum HC emissions was recorded for D100 at 11.5 N.m load (42 ppm) while the lowest recorded HC was recorded for D100 and D80B20 at 0 and 16 N.m (0 ppm) respectively.

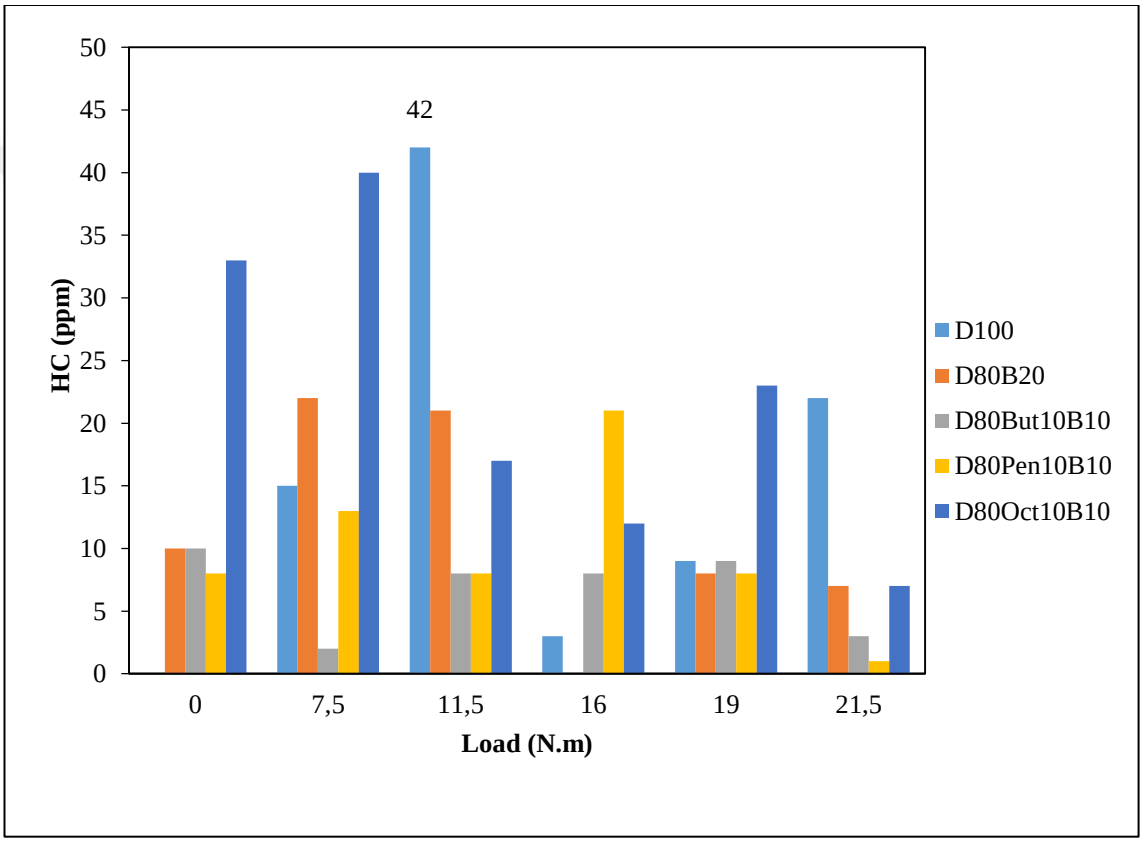


Figure 3.16. HC emissions for all fuel samples at constant speed of 1800 rpm and different loads

3.11.4. NO_x emissions

Figure 3.17 illustrates the results of NO_x emissions of D100, B20D80, B10but10D80, B10Pen10D80, and B10Oct10D80 respectively at different loads and constant engine speed of 1800 rpm. The maximum NO_x emissions was recorded for D80Pen10B10 at 7.5 and 21.5 N.m load (67 ppm) while the lowest recorded HC was recorded for D100 at 19 and 21.5 N.m (0 ppm) respectively.

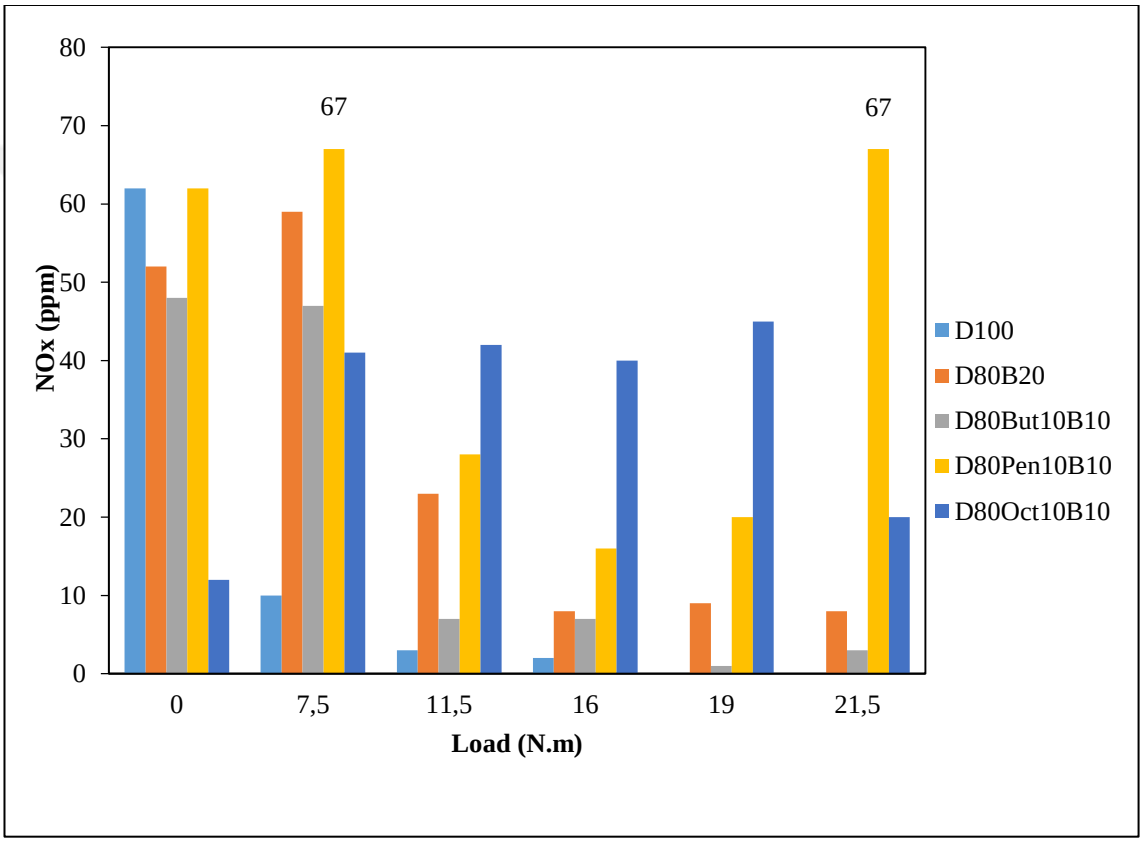


Figure 3.17. NO_x emissions for all fuel samples at constant speed of 1800 rpm and different loads

3.11.5. EGT

Figure 3.18 illustrates the results of EGT of D100, B20D80, B10But10D80, B10Pen10D80 and B10Oct10D80, respectively at different loads and constant engine speed of 1800 rpm. It can be seen that EGT increase with the increasing load for almost all tested fuels at the same speed. The maximum NO_x emissions was recorded for D80Pen10B10 at 7.5 and 21.5 N.m load (67 ppm) while the lowest recorded HC was recorded for D100 at 19 and 21.5 N.m (0 ppm) respectively.

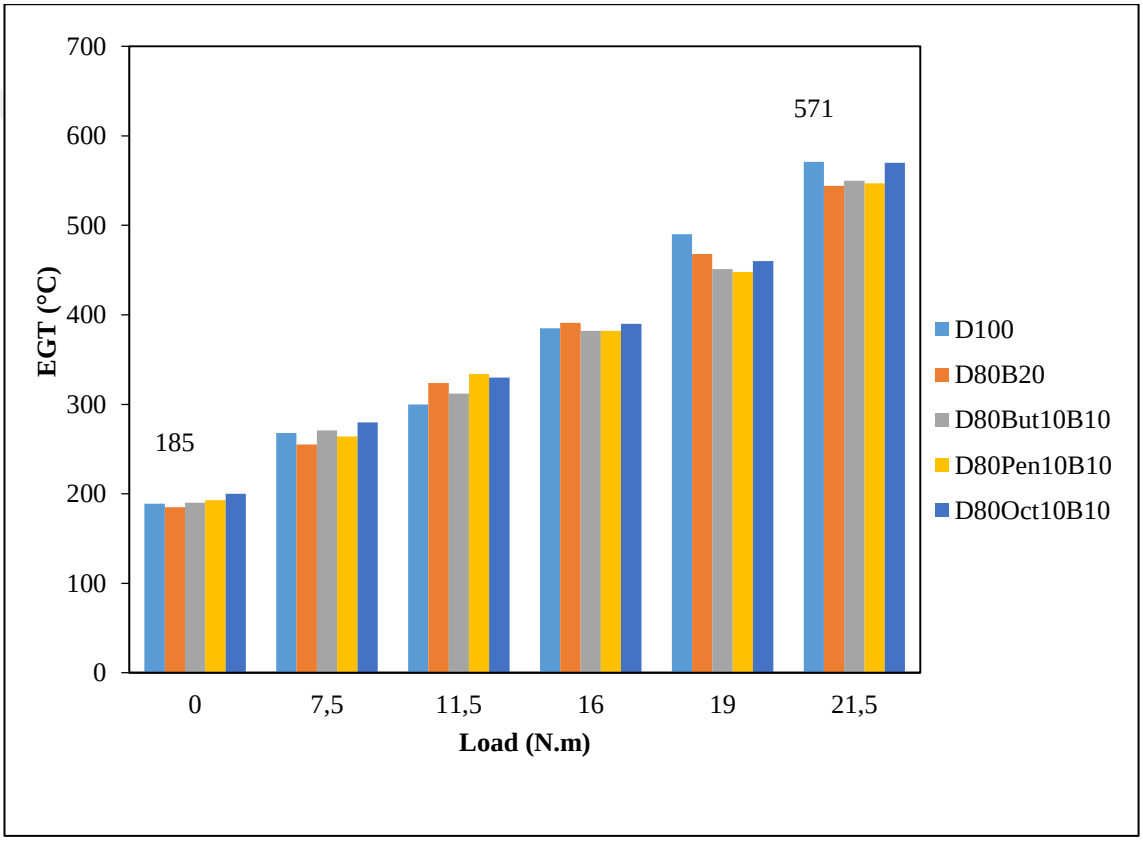


Figure 3.18. EGT for all fuel samples at constant speed of 1800 rpm and different loads

CHAPTER 4

CONCLUSIONS AND RECOMMENDATIONS

In this chapter, conclusion of the current study and some future directions were provided.

4.1. Discussion and conclusion

This work has been conducted at Alternative Fuels Research Laboratory (AFRL), Erciyes University (ERU), Kayseri, Turkey as well as the chemical laboratories of Ondokuz Mayıs Üniversitesi (OMÜ), Samsun, Turkey and engine laboratory of Al-Technalogya University, Baghdad, Iraq. The aims of this research were to recycle SCG into biodiesel. Properties of SCGOME has been found to be better than some other feed stocks. This was due to its excellent DU (110.58). With these finding; OS, CN, IV and KV of biodiesel were 5.39 h, 53.9, 106.6 g iodine/100g and 3.55 mm^2/s respectively, all of which satisfying ASTM D 6751 standards. Blending SCGOME with D100 and higher alcohols of But, Pen and Oct was the second aim of this research in which the qualities of all binary (biodiesel-diesel) and ternary (biodiesel-diesel-alcohols) blends were assessed by FT-IR, TGA, NMR, DSC and UV-vis characteristics. All of which confirmed the existence of SCGOME, D100, But, Pen and Oct in the prepared fuel samples and proved the effectiveness of these techniques as cheap, fast and reliable methods that can replace some expensive equipment that measure the properties of fuels such as cold flow properties, thermal degradation and OS.

Apart from that, some engines and emissions performance parameters such as BSFC, B_{th} (η), AFC, EGT, CO, CO_2, NO_x and HC were also studied. An increase in BSFC coupled with a decrease in EGT were observed for all binary and ternary blends compared to D100. Variation in AFC, η_{th}, CO, CO_2, HC and NO_x were observed in this

study with some marginal increase/decrease compared to D100. All of which proved that addition of Pen and Oct to the binary biodiesel-diesel blends is acceptable for application in DI CI diesel engines due to their higher CN, FP and calorific value compared to lower alcohols and closer density and kinematic viscosity to D100.

4.2. Future work and suggestions

This study conducted in-depth analyses/characterization of ternary (spent coffee grounds) blends, besides testing their effect in a single cylinder DI CI diesel engine at constant speed of 3000 rpm and three different loads of 0,7.5,11.5,16,19, and 21.5 N.m respectively. Therefore, things can be targeted in future studies for the ternary (spent coffee grounds) blends can be suggested as follow:

1. Run the engine with different injection timings and pressures.
2. Run the engine at different speeds and constant load.
3. Test the effect of some other higher alcohols such as hexanol ($C_6H_{14}O$) and decanol ($C_{10}H_{22}O$) and compare that with but, Pen and Oct.
4. Engine operation at different speed, temperatures and EGR.

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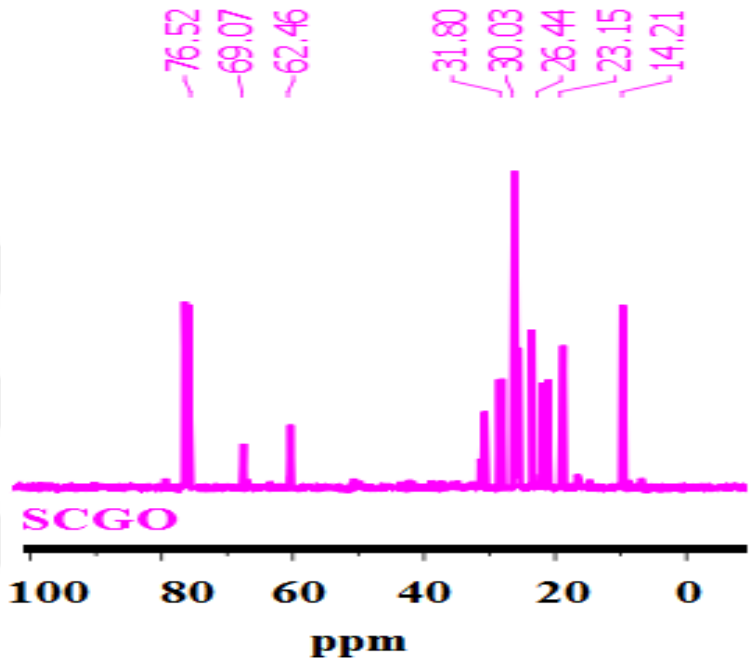
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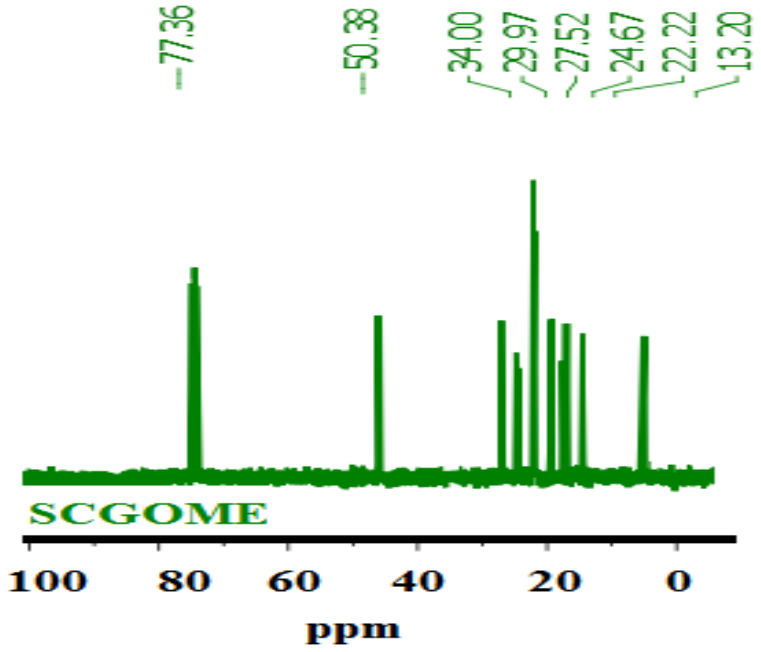
APPENDIX

APPENDIX (A) C-NMR

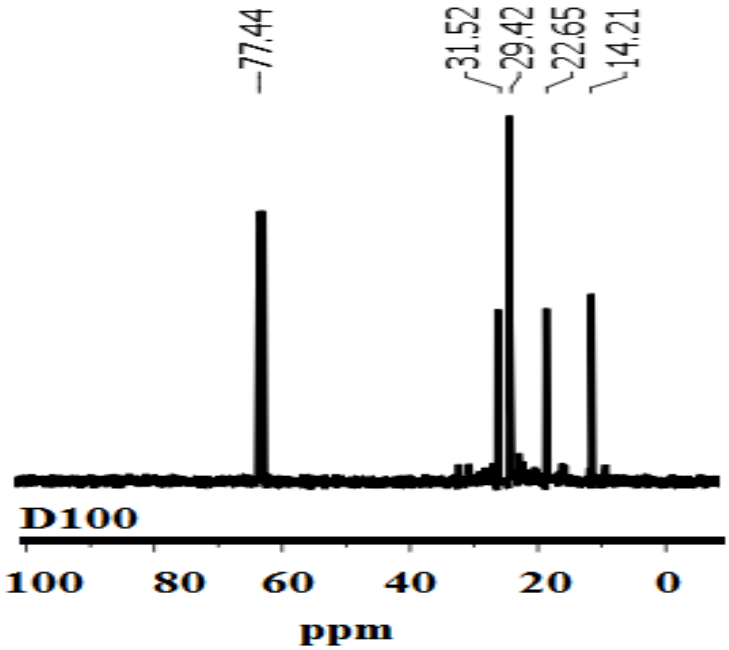
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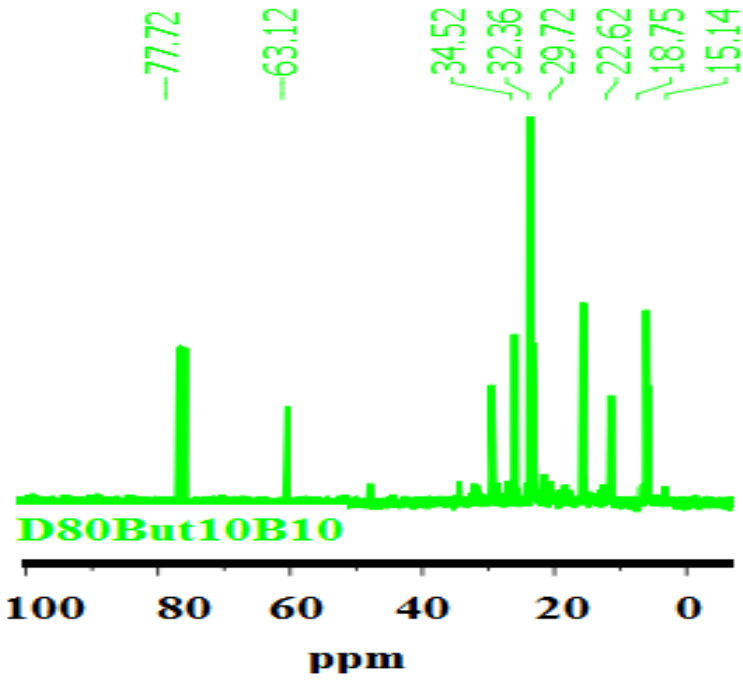
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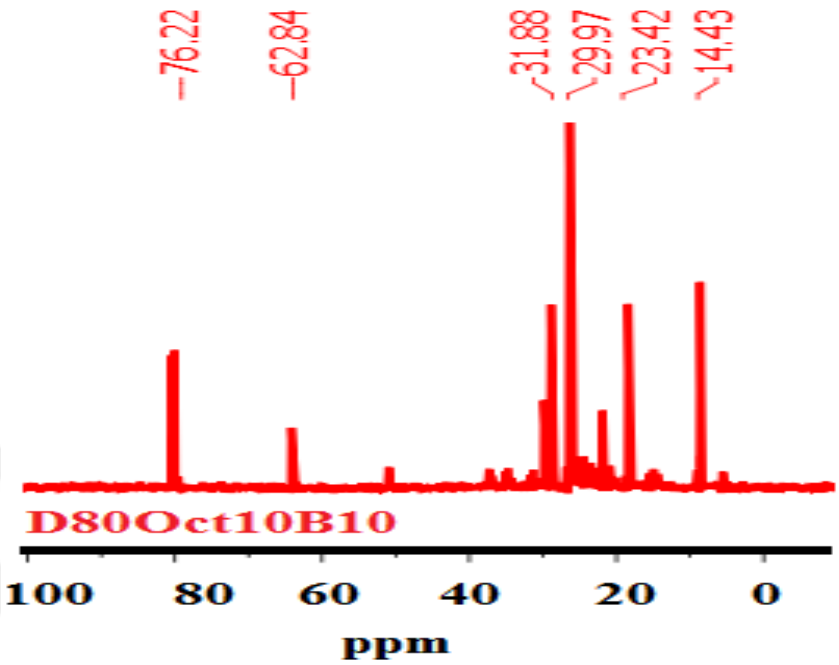
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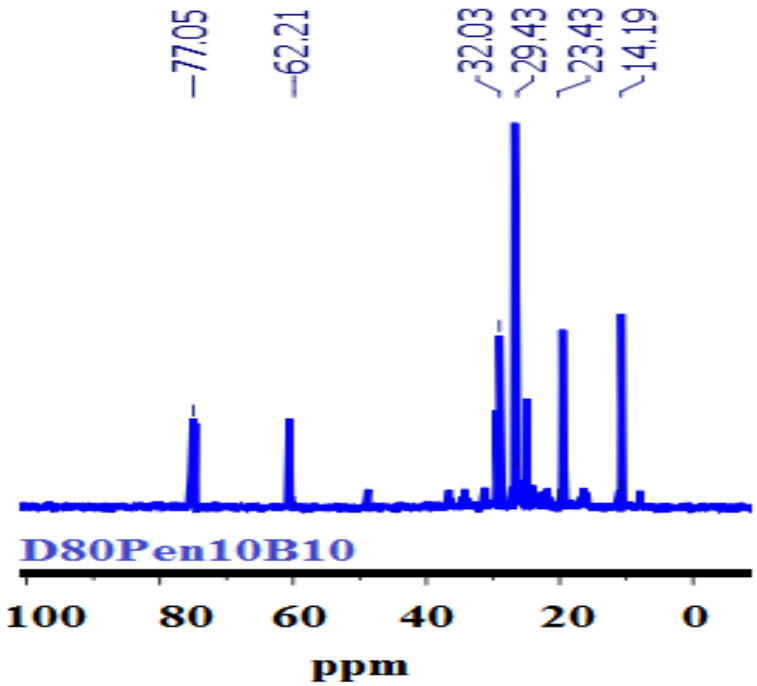
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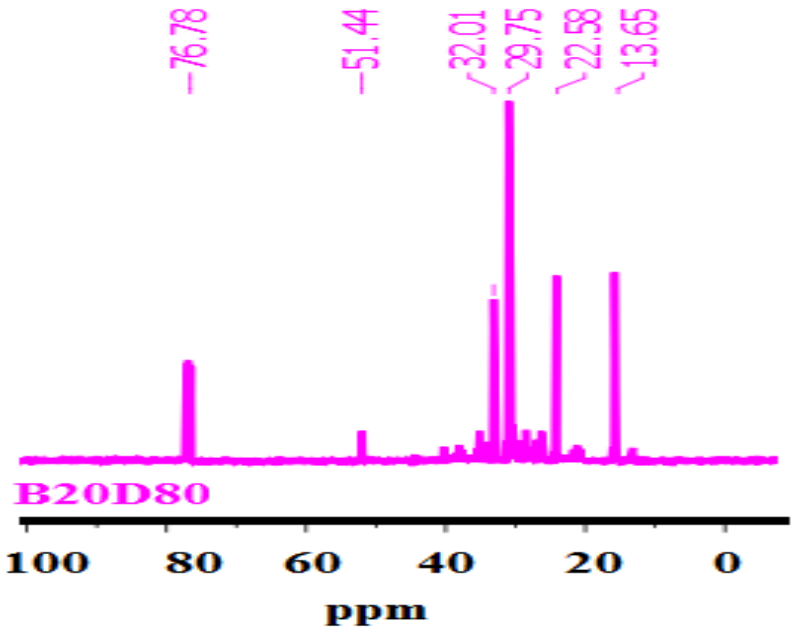
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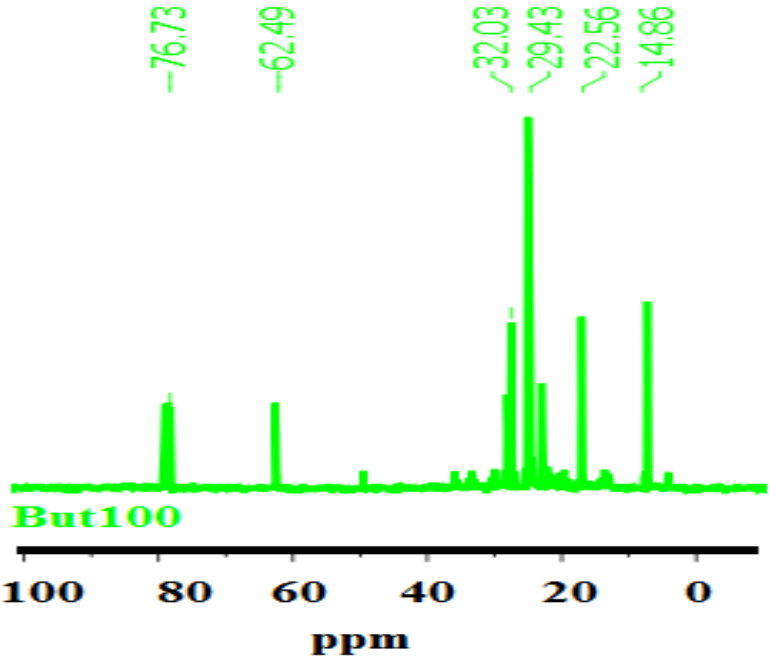
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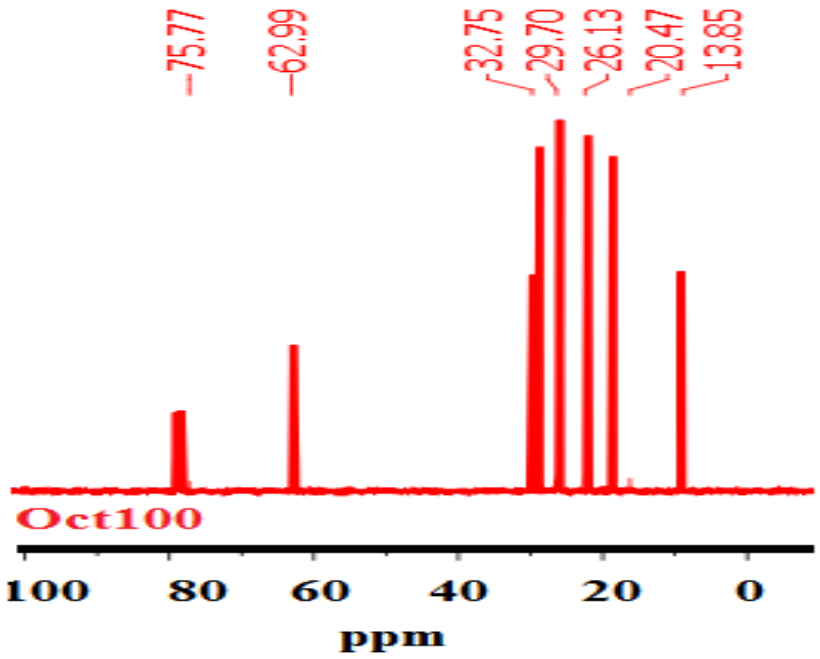
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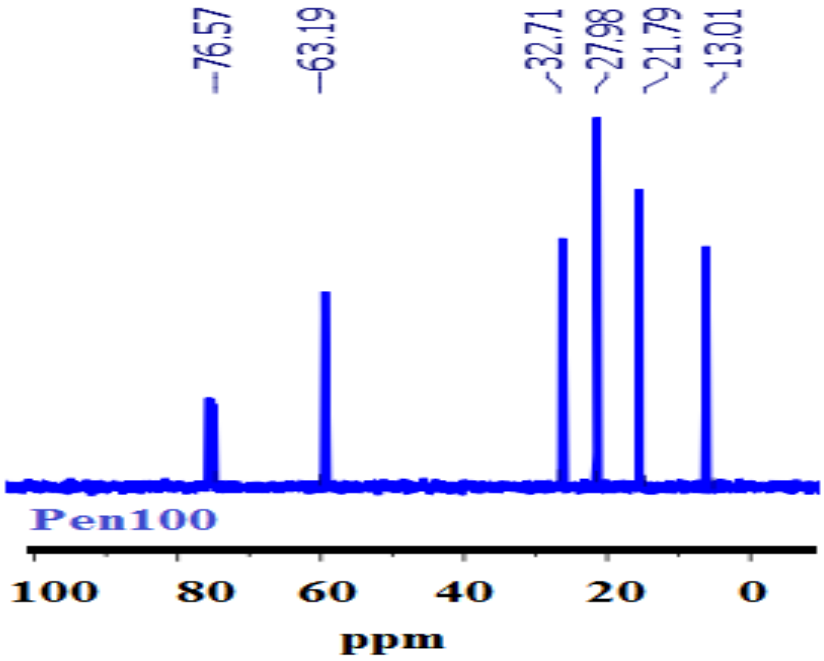
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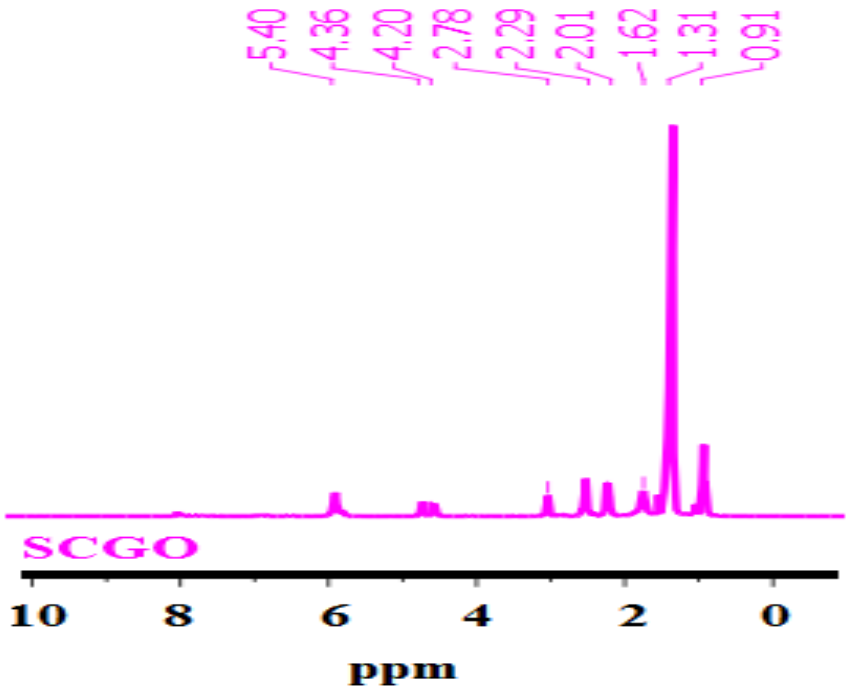


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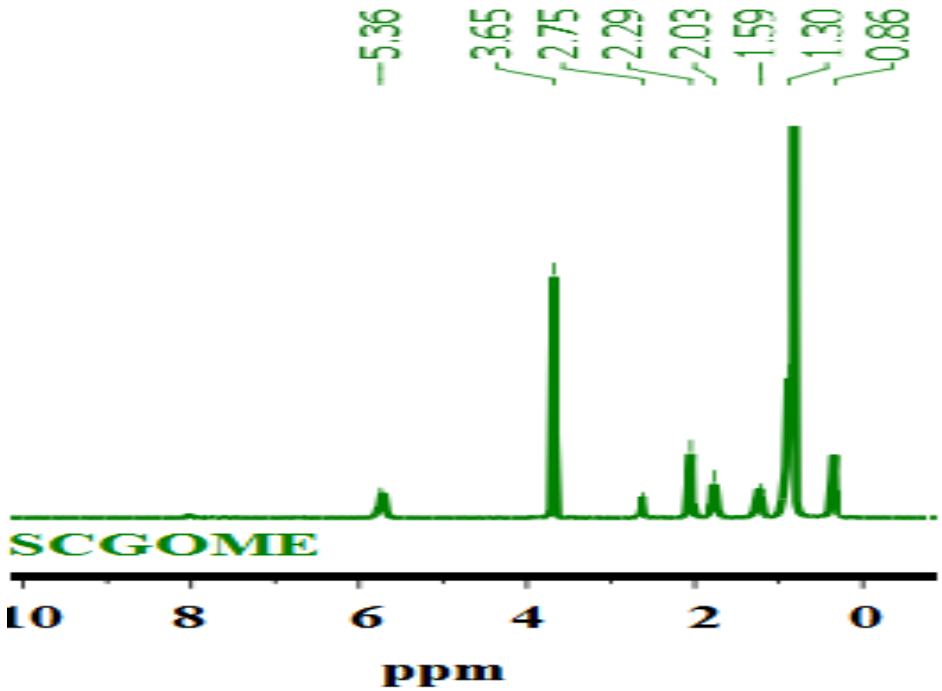


APPENDIX (B) H-NMR

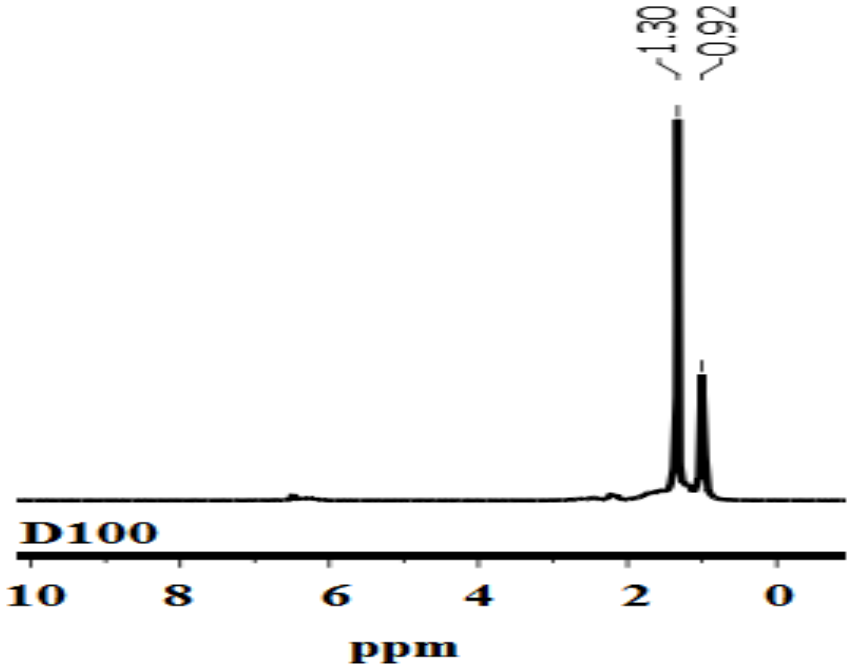
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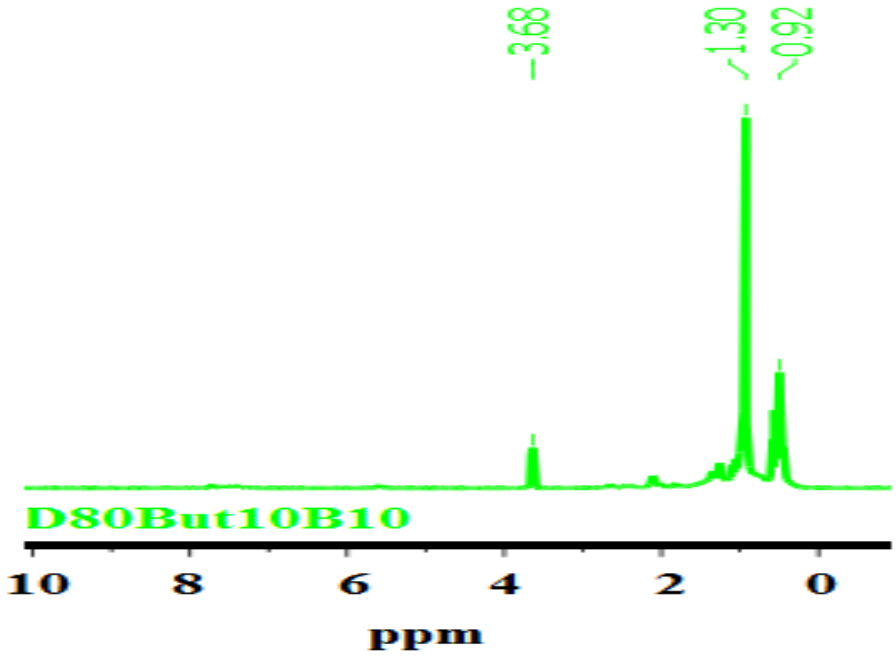
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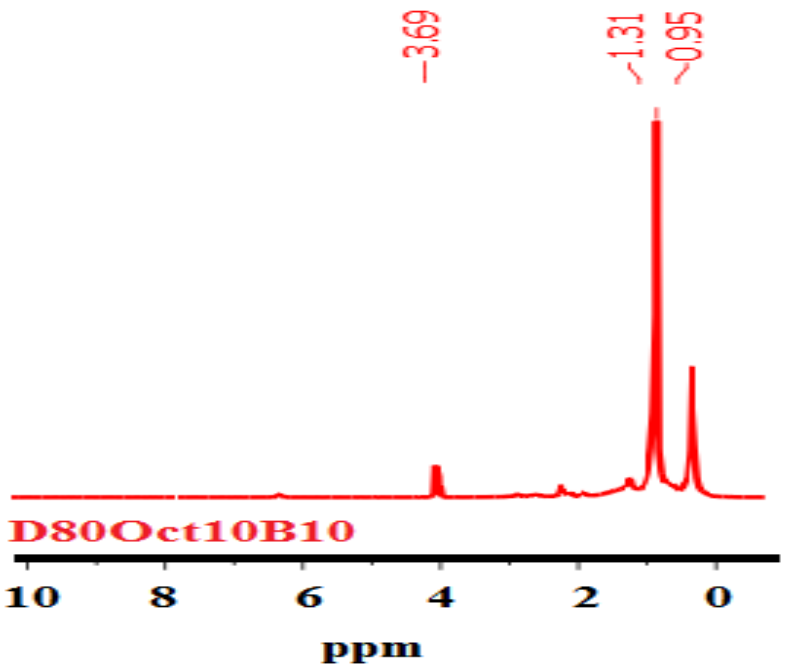
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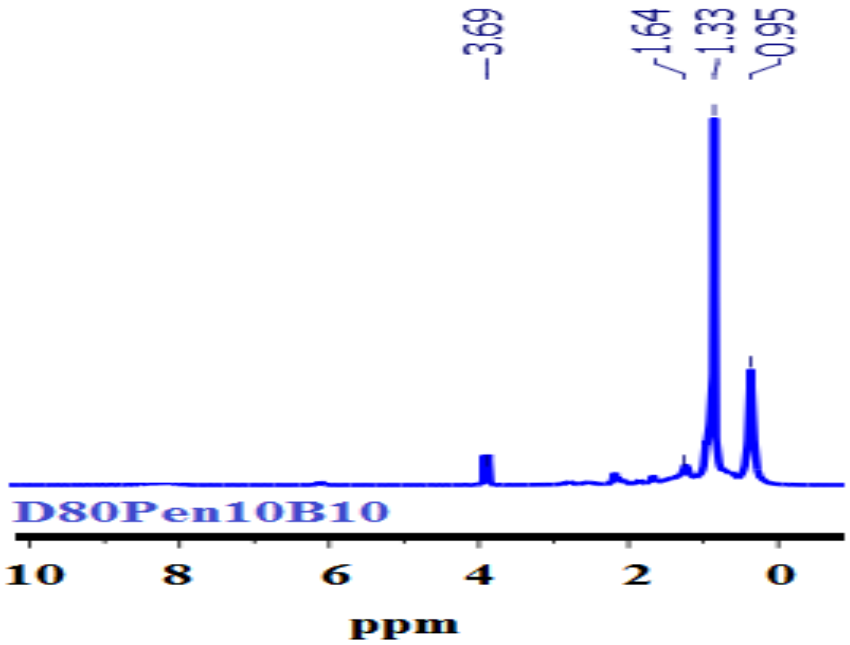
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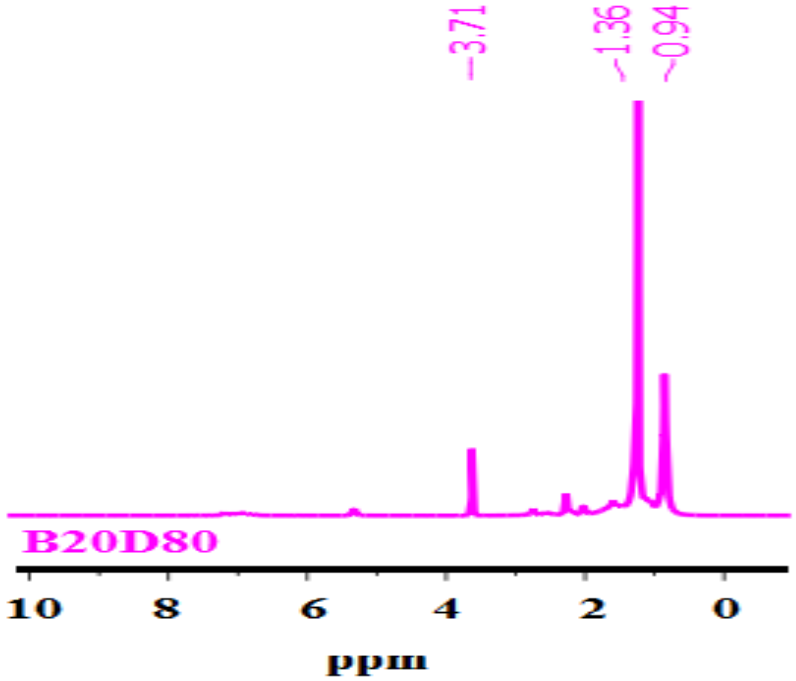
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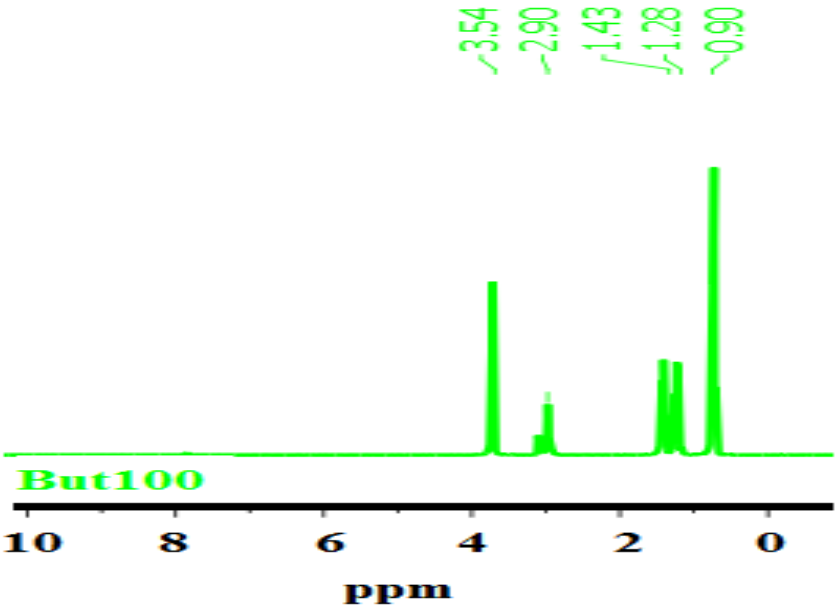
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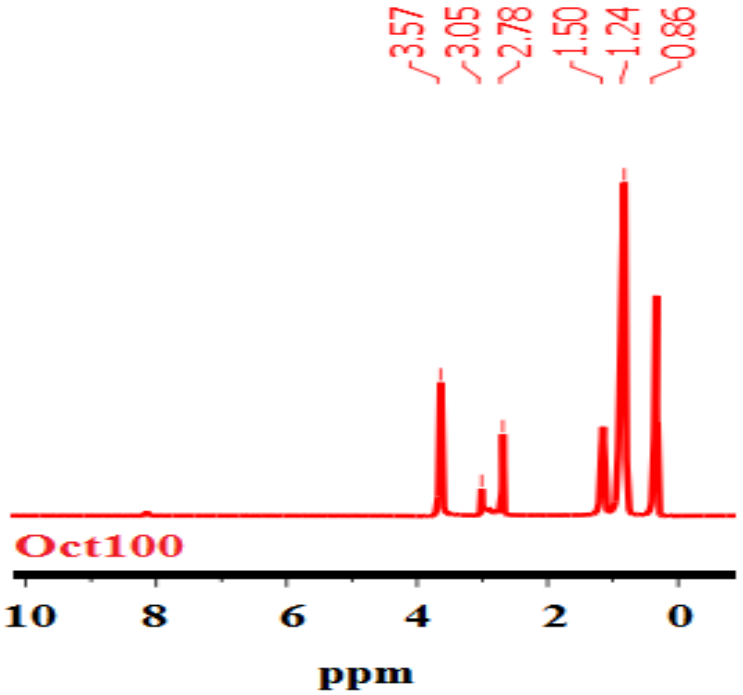
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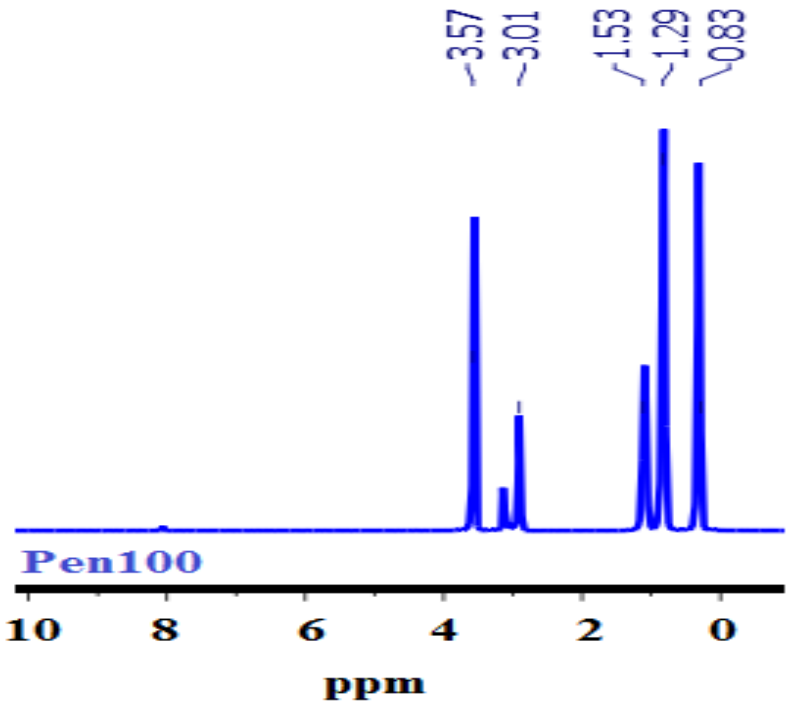
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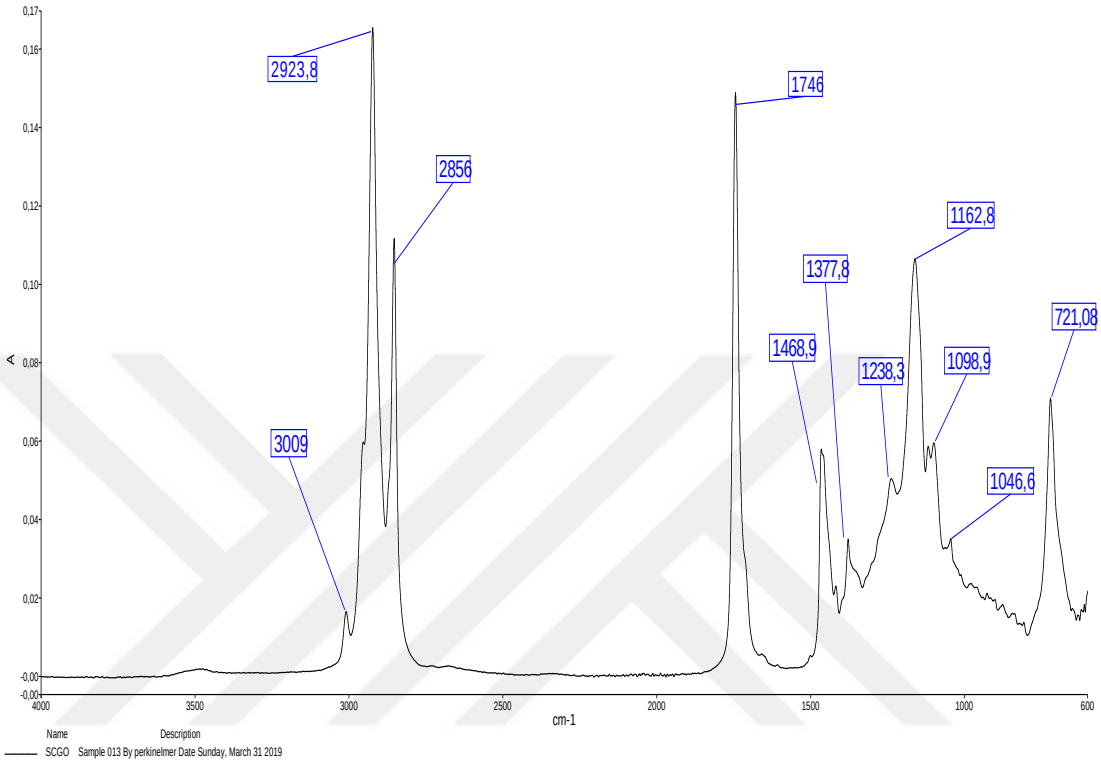


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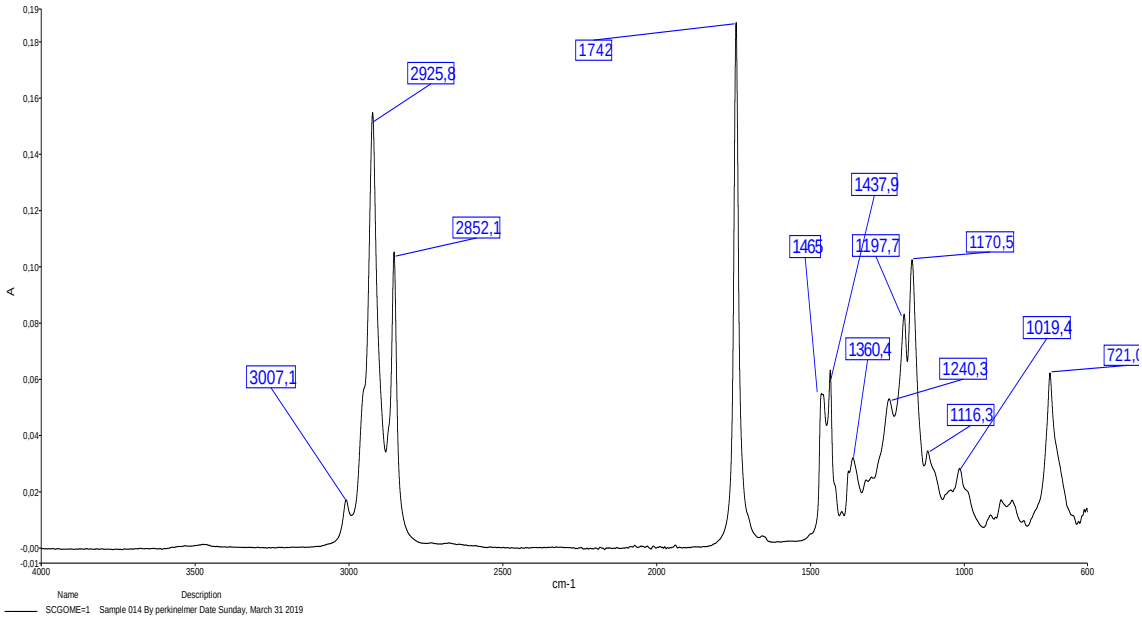


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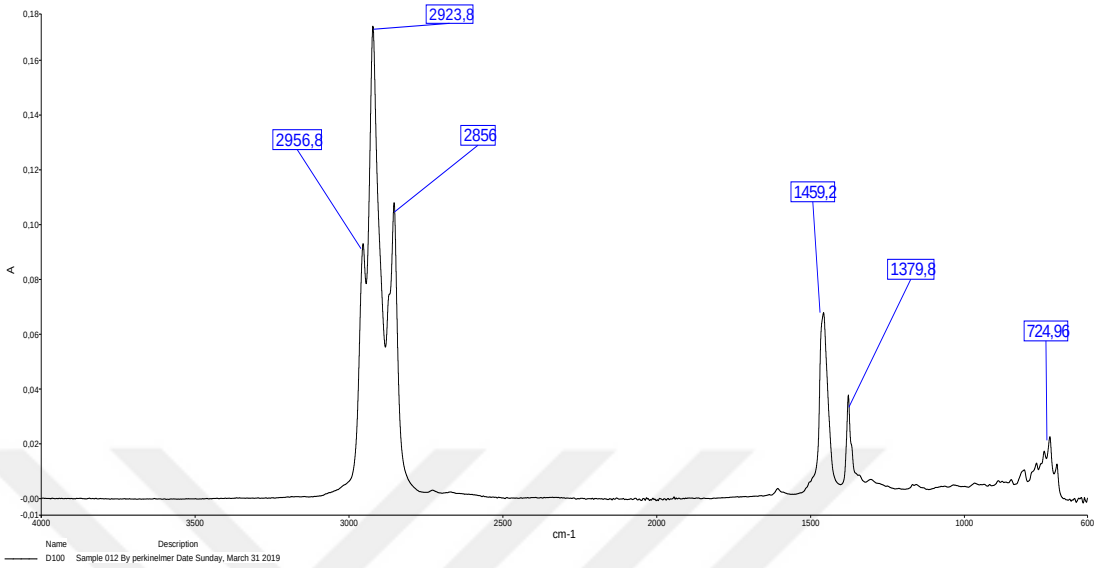
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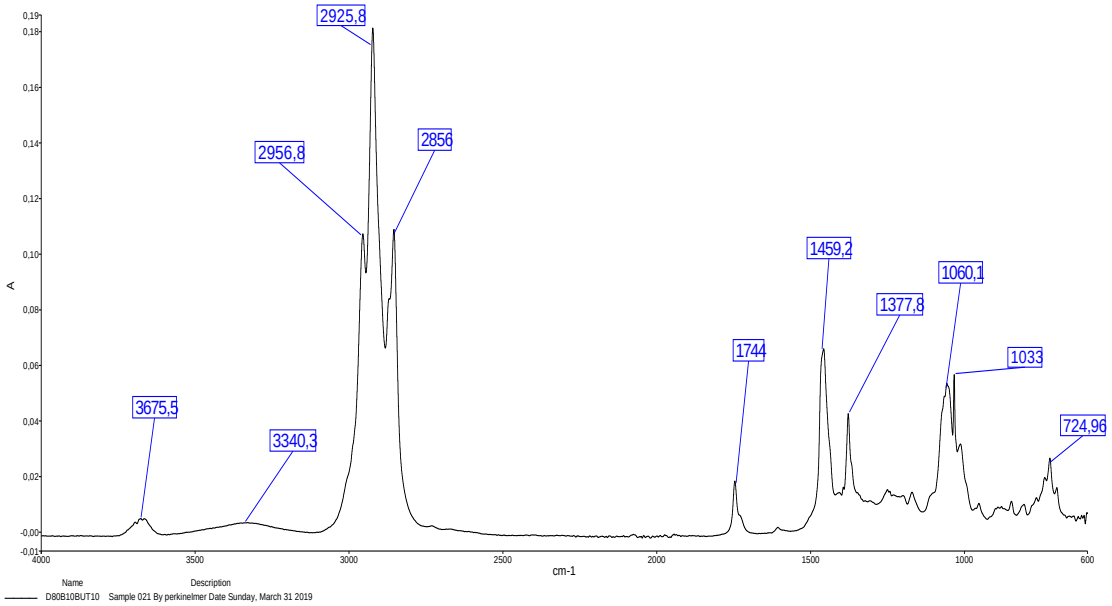
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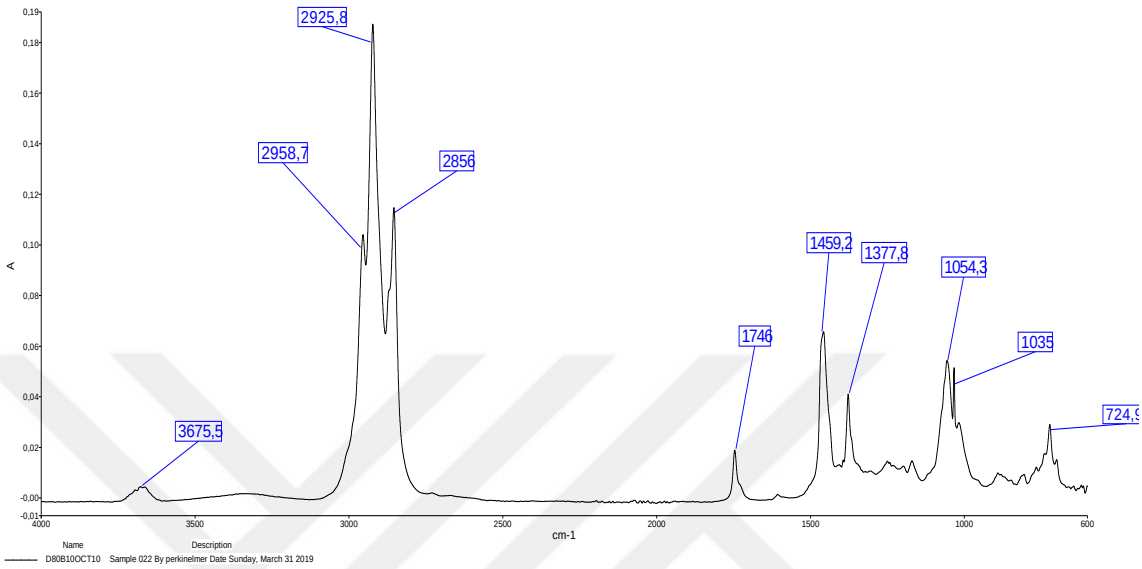
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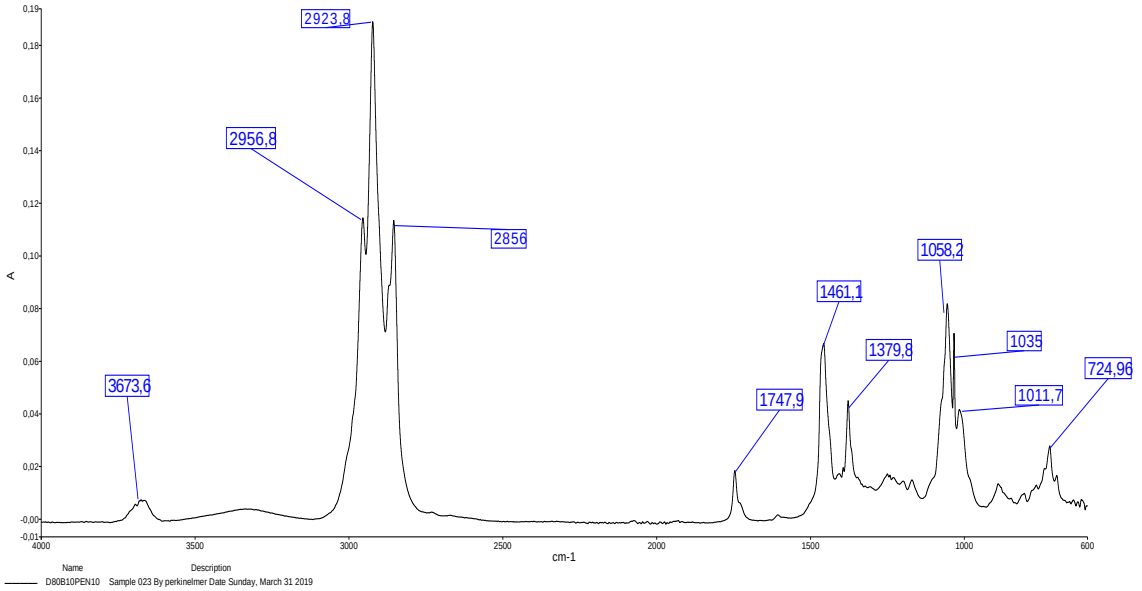
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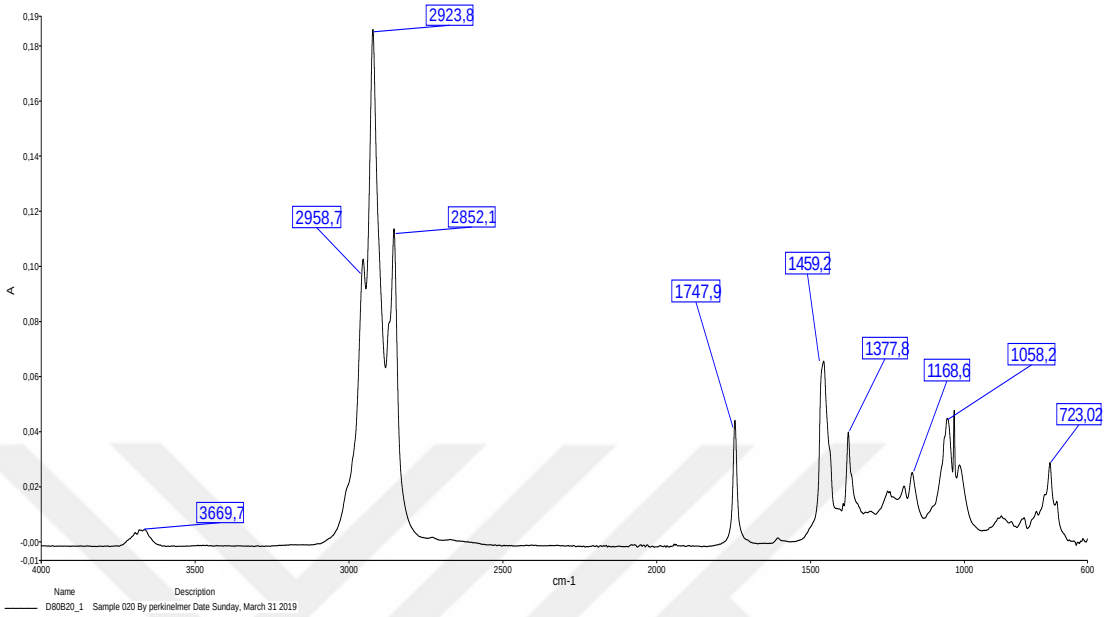
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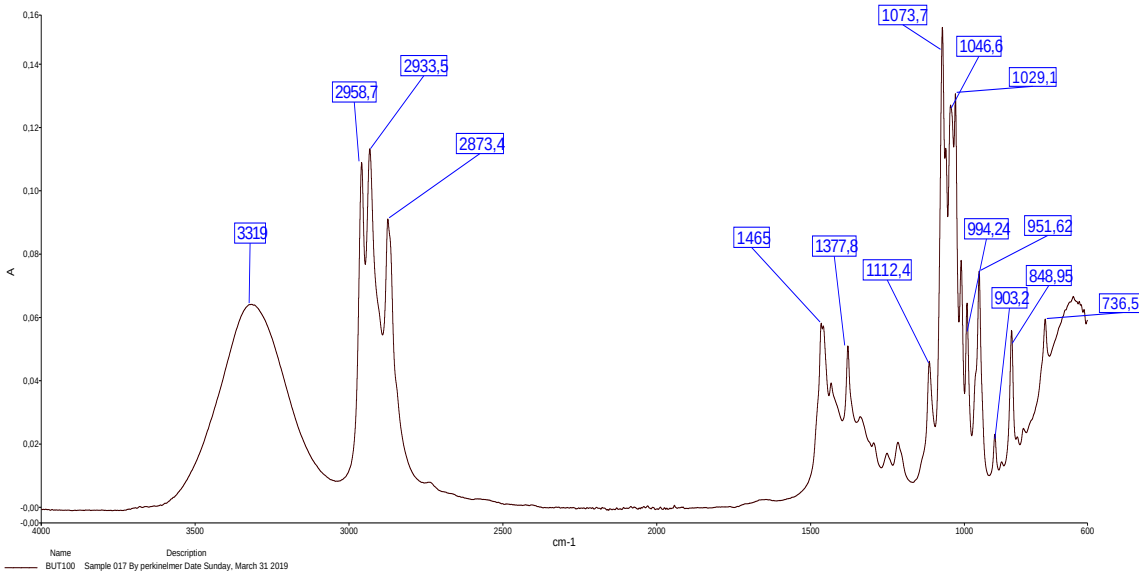
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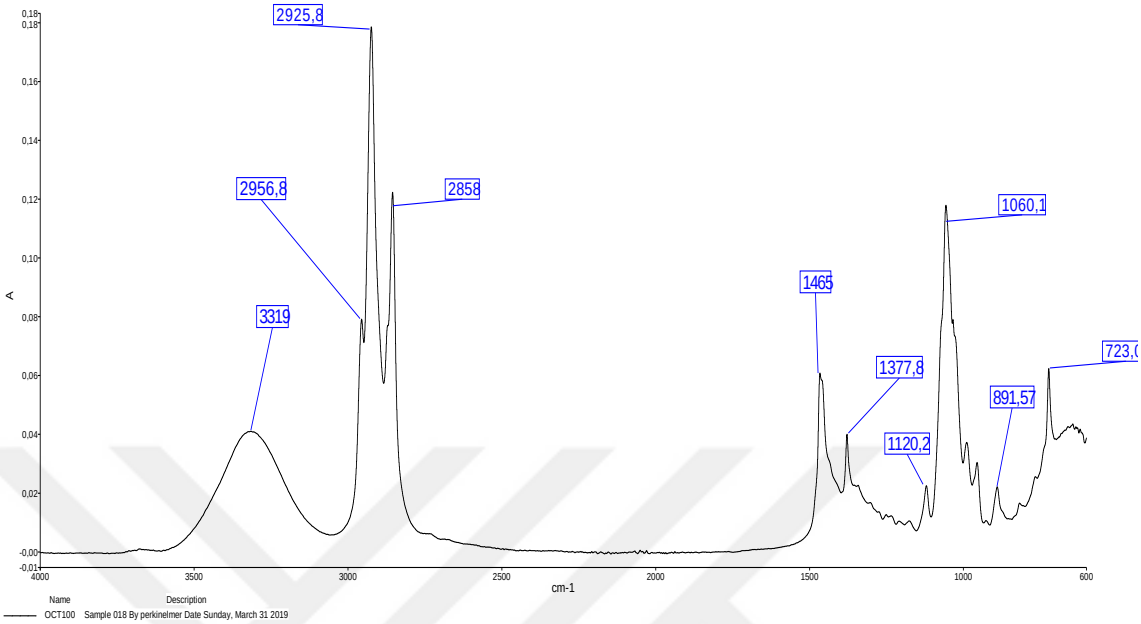
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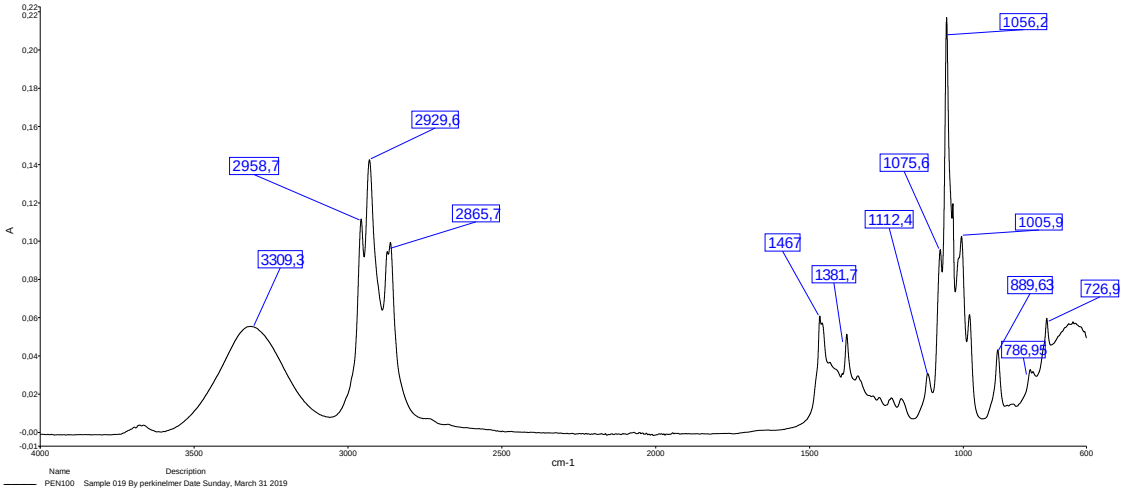
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Oct100



Pen100



CURRICULUM VITAE

PERSONAL DATA

Name and Surename:	Omar Khalid Mustafa AL-RUBAYE
Nationality:	Iraqi (IQ)
Birth Date and Place:	March 12th, 1983, Baghdad, Iraq
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EDUCATION

Degree graduation	Institute	Year
MSc	Erciyes University, Graduate School of Natural and Applied Sciences	2017
Bachelor's	Middle Technical University - Technical College Baghdad	2014
High School	Al-Maaref High school	2009

PROFESSIONAL EXPERIENCE

Year	Institute	Mission
2015/2017	Alternative Fuel Research Laboratory (AFRL)	MSc Researcher
2016	The 1st International Conference on Alternative Fuels: Future and Challenges	Organizing committee

LANGUAGES

Arabic, English, Turkish.